1988

Nuclear magnetic resonance study of the metal-nonmetal transition in lanthanum hydrides

Chii-Tzong Chang

Iowa State University

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Nuclear magnetic resonance study of the metal-nonmetal transition in lanthanum hydrides

Chang, Chii-Tzong, Ph.D.
Iowa State University, 1988
Nuclear magnetic resonance study
of the metal-nonmetal transition
in lanthanum hydrides

by

Chii-Tzong Chang

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Physics
Major: Solid State Physics

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1988
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>I. INTRODUCTION</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Metal Hydrides</td>
<td>1</td>
</tr>
<tr>
<td>B. NMR Studies of Hydrides</td>
<td>4</td>
</tr>
<tr>
<td>1. Crystal structure</td>
<td>5</td>
</tr>
<tr>
<td>2. Electronic structure</td>
<td>6</td>
</tr>
<tr>
<td>3. Hydrogen diffusion</td>
<td>6</td>
</tr>
<tr>
<td>4. Phase transition</td>
<td>8</td>
</tr>
<tr>
<td>C. Background and Motivation</td>
<td>8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>II. NUCLEAR MAGNETIC RESONANCE</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Basic Concepts</td>
<td>14</td>
</tr>
<tr>
<td>B. Spin-lattice Relaxation Mechanisms</td>
<td>18</td>
</tr>
<tr>
<td>1. Dipolar (Diffusion) contribution</td>
<td>18</td>
</tr>
<tr>
<td>2. Conduction-electron contribution</td>
<td>25</td>
</tr>
<tr>
<td>3. Paramagnetic ion contribution</td>
<td>27</td>
</tr>
<tr>
<td>4. Spin-lattice relaxation of rare-earth ions in crystals</td>
<td>33</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>III. EXPERIMENT ASPECTS</th>
<th>36</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. The NMR Pulsed Spectrometer</td>
<td>36</td>
</tr>
<tr>
<td>1. Magnet</td>
<td>36</td>
</tr>
<tr>
<td>2. Pulse programmer</td>
<td>38</td>
</tr>
<tr>
<td>3. Radiofrequency transmitter</td>
<td>39</td>
</tr>
<tr>
<td>4. The sample probe</td>
<td>40</td>
</tr>
<tr>
<td>5. Receiver</td>
<td>41</td>
</tr>
<tr>
<td>6. Data averaging and storage</td>
<td>44</td>
</tr>
<tr>
<td>7. Temperature control</td>
<td>45</td>
</tr>
<tr>
<td>B. Experimental Methods</td>
<td>49</td>
</tr>
<tr>
<td>1. Magnetization in the rotating frame</td>
<td>50</td>
</tr>
<tr>
<td>2. Spin-lattice relaxation time measurement</td>
<td>52</td>
</tr>
<tr>
<td>3. Setting up and operating the spectrometer</td>
<td>54</td>
</tr>
<tr>
<td>C. Sample Preparation</td>
<td>57</td>
</tr>
</tbody>
</table>
IV. RESULTS AND DISCUSSION

A. Pure Lanthanum Hydrides LaH$_x$, 2.0 $\leq x \leq$ 3.0

1. Electronic density of states
2. $T_{1d}$ minimum
3. Diffusion parameters
4. Coexistence of two proton resonances

B. The La$_{1-y}$Gd$_y$H$_x$ System

1. Experimental results
2. R$_{1p}$ in LaH$_{2.35}$ + 53 ppm Gd
3. R$_{1p}$ in the fast atomic diffusion regime
4. R$_{1p}$ in the spin diffusion regime

V. SUMMARY AND CONCLUSIONS

VI. REFERENCES

VII. ACKNOWLEDGMENTS

VIII. APPENDIX
I. INTRODUCTION

A. Metal Hydrides

Hydrogen with its simple electronic structure reacts with most of the elements in the periodic table. The combination of hydrogen and a metal or metalloid is called a hydride. The absorption of hydrogen by metal is usually an exothermic and spontaneous process. By heating the hydride, the hydrogen can be recovered easily. Hydrogen is considered as one of the most promising fuels for the future. It is a convenient, recyclable and environmentally acceptable energy source. Recent interest in hydrides arises partially from their potential application as a chemical means for storing and supplying hydrogen. For example, intermetallic compounds such as LaNi₅ can store hydrogen at a greater density than that of liquid hydrogen¹. Other possible applications of metal hydrides include: neutron moderators in nuclear reactors², source of high purity hydrogen³, hydrogenation catalysis⁴, etc.

It should not be considered that the presence of hydrogen in metals is always advantageous. Metal hydrides are quite brittle. In some metals the formation of hydrides which have larger volume than the corresponding metal will cause stresses and tend to crack the metal. The problem of hydrogen embrittlement also requires a deeper understanding of metal-hydrogen systems.
Binary hydrides, like most compounds, may be classified according to the nature of the metal-hydrogen bond into three major categories. These are the covalent, ionic and metallic hydrides. These hydride groups show different physical properties. The rare-earth hydrides (except Eu and Yb) and the actinide hydrides are usually classified with the metallic hydrides. They generally exhibit metallic properties such as high thermal conductivity and electrical conductivity (except the higher hydrides of the rare earths), luster and hardness. However, unlike metals they are very brittle.

The electronic structure of metallic hydrides has been the subject of much interest and controversy. In the early studies, two extreme models based on rigid bands were proposed to account for the observed electronic properties. In the proton model, hydrogen is assumed to donate its electron to the metal bands leaving a screened proton in the metal sublattice and, conversely, in the anion model hydrogen accepts an electron from the metal to form a hydride anion and metal cation. Switendick first used the augmented plane wave (APW) method to calculate the band structure of several transition metal hydrides. In his non-rigid band model, the protons contribute along with the metal ion cores to the electrostatic potential in which the delocalized electrons move. In the hydrides of trivalent rare-earth metals, a new band forms for each hydrogen atom in the unit cell and an
energy gap arises between this low lying band and the higher metal bands. For the dihydrides, the Fermi level is moved into the conduction band and the material is metallic. The trihydride is a semiconductor since the three new bands accommodate all of the six valence electrons. These band structure calculations predict some experimental results of metallic hydrides, but there remain some difficulties with the evaluation of electronic properties for most metallic hydrides.

In metallic hydrides, hydrogen is usually, but not always, found in the tetrahedral or octahedral interstitial sites of closed-packed arrays of the metal sublattice. In most cases the metal sublattice of the hydride is different from that of the parent metal, supporting the idea that metal hydrides are not interstitial solid solutions. In the few cases of cerium, nickel, actinium and palladium, the metal sublattice remains unchanged on hydriding, but they exhibit discontinuous increases in lattice parameter. Occupation of all the octahedral sites in face-centered cubic (fcc) metals gives the composition MH and the NaCl type structure which is found in PdH. Occupation of all the tetrahedral sites gives the composition MH₂ and the fluorite (CaF₂) structure. This structure is found in the majority of rare earth group III (Sc, Y, La) and group V (V, Nb) dihydrides. Simultaneous occupation of both tetrahedral and octahedral sites in the fcc
lattice gives the composition M\textsubscript{H\textsubscript{3}} and the cubic BiF\textsubscript{3}-type structure which is found in light rare earth (La, Ce, Pr and Nd) trihydrides. The metal sublattice in the rare earth trihydrides YH\textsubscript{3}, GdH\textsubscript{3} through TmH\textsubscript{3}, and LuH\textsubscript{3} is hexagonal, the same as the parent metals, but there is also a dihydride phase with the fcc metal sublattice in these systems. Unlike ionic hydrides, a large number of metallic hydrides do not always have stoichiometric compositions.

B. NMR Studies of Hydrides

Nuclear magnetic resonance (NMR) is an effective tool in the study of metal hydrides. Both continuous wave NMR and pulsed NMR can be used to investigate hydrogen locations and dynamic aspects of metal hydrides. In continuous wave NMR, the sample is continuously irradiated with rf radiation; a spectrum is then obtained as the magnetic field is slowly changed and the absorption of energy by the sample is recorded. In pulsed NMR, the sample is irradiated with high power rf pulses and the response to the pulses is recorded. The observed NMR signal depends on the selected nucleus. Most NMR studies have been done on the proton (\textsuperscript{1}H) because it usually gives the strongest signal due to its relatively large magnetic moment and nearly 100% natural abundance. Studies of deuterides which contain deuterons (\textsuperscript{2}D) with spin 1 and a small electric quadrupole moment can give useful information.
not available from the proton studies. In addition, studies of the metal nuclei may give information on the symmetry of the metal positions and the electronic structure. The potential of NMR in the investigation of the properties of metal hydrides has been reviewed by Cotts\(^9\) and Barnes\(^{10}\). A brief summary of the applications of NMR to the study of hydrides will now be given.

1. **Crystal structure**

   In solids at low temperatures, each resonant nucleus is coupled with neighboring nuclei. This effectively broadens the resonance lines. The proton resonance linewidth is determined by the magnetic dipolar coupling between the protons, and between the protons and metal nuclei. The application of NMR to structural studies is based on the comparison of calculated and observed values for the second moment which is the mean square linewidth and is closely related to the local structure\(^{11}\). The second moment can also be obtained using pulsed NMR methods at low temperature or from the minimum in the spin-lattice relaxation time. Since NMR is sensitive to the local structure, it can give unique information in systems in which certain interstitial sites are occupied. In addition, since deuterons and many of the host metal nuclei possess electric quadrupole moments, the interaction of such quadrupolar nuclei with the gradient of
the crystalline electric field has also proved to be a valuable NMR probe in establishing hydrogen locations and site symmetries.

2. Electronic structure

The Knight shifts observed for the metal nuclear resonances in metal hydrides may give valuable information on electronic structures. Knight shifts are caused by the coupling between the nucleus and the spin of the electrons. The electrons at the Fermi level which are polarized by the applied magnetic field contribute an additional magnetic field at the position of the metal nucleus and the resonance signal is therefore shifted. The Knight shift in most metals is toward higher frequencies and is directly proportional to the density of states of the electrons at the Fermi level. The conduction electrons also give rise to spin-lattice relaxation at all temperatures in metals. According to the Korringa relation, \((T_{1}T)^{-\frac{1}{2}}\) is a constant and is also proportional to the density of states at the Fermi level (see Section B of Chapter II).

3. Hydrogen diffusion

At any finite temperature the hydrogen in a metal hydride is not at rest but is constantly in motion. At extremely low temperatures, this motion may be that of the lattice
vibrations, however, as the temperature is increased hydrogen atoms gain more energy and diffusion may occur. The onset of hydrogen diffusion has a clear effect on NMR signals. As diffusion occurs, the proton resonance line narrows due to the partial averaging out of the dipolar interaction when the mean dwell time of a proton on a lattice site becomes shorter than the inverse of the line width\(^1\). The mean dwell time is usually assumed to be given by an Arrhenius equation,

\[
\tau_0 = \tau_{00} \exp\left(\frac{E_a}{k_B T}\right)
\]

where \(E_a\) is the activation energy for the diffusive motion, \(\tau_{00}\) is a constant prefactor, \(k_B\) is Boltzmann's constant and \(T\) is the absolute temperature. From line narrowing measurements, the activation energy and \(\tau_{00}\) can be determined. Much of the study of hydrogen diffusion using NMR is through measurements of various relaxation times; spin-lattice relaxation time \(T_1\), spin-spin relaxation time \(T_2\), and the rotating from spin-lattice relaxation time \(T_{1\phi}\).

From measurements of the spin echo attenuation in a magnetic field gradient, it is possible to determine the self diffusion coefficient directly\(^1\). For diffusion in cubic metals, the diffusion coefficient \(D_a\) is related to the mean dwell time \(\tau_0\) by

\[
D_a = \left(\frac{f_\tau \left< \ell^2 \right>}{6\tau_0}\right)
\]

where \(\left< \ell^2 \right>\) is the mean squared jump distance of hydrogen and \(f_\tau\) is a tracer correlation factor for successive jumps\(^1\). By
combining $D_a$ and $\tau_D$ (from spin-lattice relaxation measurements), it is possible to determine the mean jump distance and therefore obtain information about the diffusion path.

4. Phase transition

The temperature dependence of the different NMR parameters can be used to determine the phase diagram of the metal-hydrogen system. Although the lineshape of the proton spectrum is generally insensitive to phase transitions unless the phase change occurs in the temperature range of motional narrowing, changes in the proton spin-lattice relaxation time can give information on the phase diagram. For example, in tantalum hydrides large discontinuities in the $T_1$ versus temperature curve are observed, and two $T_1$'s are seen in two-phase regions\textsuperscript{16}. In addition, the deuteron resonance spectra also provide direct information on the phase diagram\textsuperscript{17}.

C. Background and Motivation

Lanthanum reacts exothermically with hydrogen to form nonstoichiometric hydrides with a maximum of 3 hydrogen atoms per lanthanum atom\textsuperscript{18}. At hydrogen concentrations $[H]/[\text{La}]$ less than 2, coexistence of the $\alpha$ and $\beta$ phases occurs. The $\beta$-phase lanthanum hydride LaH$_x$ exists from $x \geq 1.9$ to $x = 3$, and has a structure based on that of CaF$_2$ with the metal atoms
located on an fcc lattice. Hydrogen occupies predominantly the interstitial sites with tetrahedral symmetry. As more hydrogen is added, a second type of interstitial site with octahedral symmetry is filled (Figure 1.1). X-ray diffraction\(^9\) has shown that for \(T \leq 250\) K, \(\text{LaH}_x\) undergoes a slight tetragonal distortion of the metal lattice in the composition range \(2.65 \leq x \leq 2.90\). Neutron diffraction measurements at \(295\) K indicate that the deuterium atoms in \(\text{LaD}_x\) do not occupy the center of the octahedral sites but are randomly displaced along \(<111>\) directions\(^{20}\). In a more extensive neutron-diffraction study of \(\text{LaD}_x\), Didisheim et al.\(^21\) suggested the occurrence of ordering of the deuterium atoms on off-center positions in the octahedral sites. NMR studies by de Groot et al.\(^22\) on \(\text{LaD}_x\) (\(2.28 \leq x \leq 3.00\)) confirmed the formation of a deuterium superlattice.

Due to the numerous changes in physical properties as functions of hydrogen concentration and temperature, the lanthanum hydride system has attracted considerable attention in the past. Particularly, some of the early studies already focused on the apparent metal-nonmetal transition in this system. The dihydrides \(\text{LaH}_2\) exhibit metallic conductivity due to the occurrence of overlapping energy bands, but as the ratio \([\text{H}]/[\text{La}]\) approaches 3 the bands are shifted considerably and semiconducting (or insulating) behavior is expected\(^7\). Libowitz\(^23\) has given a review of electrical resistivity
Figure 1.1 The conventional fcc unit cell shows the positions of host metal (La) atoms and tetrahedral (T) and octahedral (O) hydrogen sites. The tetrahedral hydrogen is located at the center of a tetrahedron formed by its four nearest host atoms. Octahedral sites have six nearest host atoms forming a regular octahedron. There are two T-sites and one O-site for each metal atom.
measurements for a number of rare-earth hydrides. Upon the addition of hydrogen to the dihydride, the resistivity increases monotonically. At concentration near $x = 2.8$, the resistivity increases sharply, and the increase is identified with a metal-semiconductor transition. In addition to this compositional transition, a temperature-dependent metal-semiconductor transition occurs near $250 \text{ K}$ for $\text{CeH}_2.7-2.8$\textsuperscript{23}. Photoemission studies of $\text{LaH}_x$ at $300 \text{ K}$ indicate that the material behaves like a small band-gap semiconductor near $x = 2.89$\textsuperscript{24}. More recently, heat-capacity measurements at low temperatures for $\text{LaD}_3$ and $\text{LaH}_3$ show no evidence for an electronic contribution\textsuperscript{25}. In $\text{LaD}_3$, four sharp heat-capacity anomalies were found at 211, 230.5, 233.5, and 274.3 K, while in $\text{LaH}_3$ two slightly broader peaks were observed at 241 and 270 K. The lowest transition in both $\text{LaD}_3$ and $\text{LaH}_3$ is thought to be a metal-to-semiconductor transition. Self-consistent band structure calculations by Misemer and Harmon\textsuperscript{26} predict that in the trihydride a small gap ($\sim 0.2 \text{ mRy}$) opens up at the Fermi level.

Despite the fact that nuclear magnetic resonance was first utilized in studies of the lanthanum hydrides about twenty-five years ago\textsuperscript{27}, almost no further NMR investigations of this system have been reported. More recent measurements of the proton spin-lattice relaxation time in $\text{LaH}_2.9$ followed a Korringa relation down to $77 \text{ K}$\textsuperscript{28}, however, Phua et al.\textsuperscript{29}
have very recently demonstrated the marked effect of paramagnetic impurities on the spin-lattice relaxation time and now believe the apparent Korringa behavior may be due to such impurities. Because of the strong effects of residual impurity ions on the proton $T_1$, determinations of the Korringa product and hydrogen diffusion parameters can err significantly. Now, with samples of higher purity, the "true" behavior of the lanthanum hydride system is under investigation. On the other hand, since the effects of the paramagnetic impurities are now thoroughly understood, they are found to be useful as an additional method of exploring other phenomena. In this work we used the Gd$^{3+}$ ion to probe the occurrence of the metal-nonmetal transition in lanthanum hydrides.

In the work reported here, we have studied both the temperature and composition dependence of the proton $T_1$ in LaH$_x$ samples covering the range $2.0 \leq x \leq 3.0$. Wide-line measurements of the proton resonance were made for many of the same samples. In addition, $T_1$ measurements were made on a series of lanthanum hydrides containing controlled low levels of gadolinium impurity. A brief review of the theoretical background relating to nuclear magnetic resonance, including the various relaxation mechanisms, is given in Chapter II. A description of the apparatus used in this work, details of the experimental procedures and sample preparation methods are
presented in Chapter III. Finally, experimental results and discussion are given in Chapter IV.
II. NUCLEAR MAGNETIC RESONANCE

A. Basic Concepts

Magnetic resonance is a phenomenon found in systems that contain nuclear or electronic magnetic moments. Many atomic nuclei have a non-zero spin angular momentum $\hbar I$ (integer or half integer in units of $\hbar$, Planck's constant divided by $2\pi$) and a magnetic moment $\mu = \gamma \hbar I$, where $\gamma$ is the gyromagnetic ratio. It is these moments that make nuclear magnetic resonance possible.

A sample containing a system of nuclear spins may be examined from two viewpoints: microscopic and macroscopic. From the microscopic point of view, our attention is focused on a particular nuclear spin. When the sample is placed in an external magnetic field $\vec{H}$, each magnetic moment $\vec{\mu}$ experiences a torque $\vec{\mu} \times \vec{H}$. According to the classical theory of electromagnetism, the motion of the magnetic moment is described by the equation for the rate of change of angular momentum,

$$\frac{d(\vec{I}\hbar)}{dt} = \vec{\mu} \times \vec{H}. $$

Since $\vec{\mu} = \gamma \hbar \vec{I}$, we get

$$\frac{d(\vec{\mu})}{dt} = \vec{\mu} \times \gamma \vec{H}. $$

This equation, which holds regardless of whether $\vec{H}$ is time dependent or not, describes the precession of the spin around the field $\vec{H}$. In a static field $\vec{H} = \vec{H}$, constant in time, the
spin precesses with an angular frequency $\omega_0$, where $\omega_0 = -\gamma H_0$ is called the Larmor frequency of the spin in the applied field $H_0$.

The quantum mechanical description of a spin in a static field starts from the Hamiltonian:

$$\mathcal{H}_0 = -\mu \cdot H_0 = -\gamma H_0 I_0.$$

Taking the field to be along the z-direction, we find

$$\mathcal{H}_0 = -\gamma H_0 I_z.$$

The allowed energies are

$$E_m = -\gamma H_0 m, \quad m = I, I-1, \ldots, -I.$$  (2-2)

Therefore the orientation of a precessing spin is quantized, the number of allowed orientations being $2I+1$.

If a small rf magnetic field $H_1$ is applied perpendicular to the static field $H_0$, the coupling of this spin with the rotating field $H_1 = i H_1 \cos \omega t + j H_1 \sin \omega t$ can be described by a perturbation Hamiltonian,

$$\mathcal{H}_1 = -\gamma H_1 (I_x I_x + I_y I_y) = -(1/2) \gamma H_1 (I_+ e^{-i\omega t} + I_- e^{i\omega t}).$$

Because of the properties of the operators $I\pm$, $\mathcal{H}_1$ has matrix elements only between states for which $m$ differs by one unit. Consequently the allowed transitions are between states separated by an energy interval $\Delta E = \gamma H_0 = \hbar \omega$, if $\omega = \omega_0$.

The condition $\omega = \omega_0$ is needed to satisfy the conservation of energy, the change in energy $\hbar \omega_0$ of the spin being compensated by the energy $\hbar \omega$ of the photon which is absorbed or emitted.

To completely describe the motion of the nuclear spin in
a magnetic field it is necessary to take into account its interactions with nearby nuclei and with the surroundings. A simpler approach is to consider the macroscopic magnetic properties of the sample. Instead of focusing attention on an individual magnetic moment $\tilde{\mu}$, we can study the bulk magnetization $\vec{M}$ which is the magnetic moment per unit volume defined as $\vec{M} = \frac{1}{V} \sum_{i} \mu_i$.

Relaxation phenomena are important in the study of nuclear magnetism. It is owing to the relaxation mechanisms that the nuclear spins can "feel" the temperature of the lattice and come to equilibrium with it. At equilibrium, nuclei are distributed among the energy levels of Equation 2-2 according to a Boltzmann distribution. As a consequence of this distribution a net nuclear magnetization

$$M = N g I (I+1) H_0 / (3k_B T)$$

appears in a static field $H_0$. After any process that disturbs this distribution (e.g., turning on or off the static magnetic field), the nuclear spin system does not return to equilibrium with its surroundings (the lattice) immediately, but over a characteristic time $T_1$, the spin-lattice relaxation time. This is because the recovery is governed by the rate at which energy can be transferred between the spin system and the lattice. Now if a small rf field $H_1$ at resonant frequency $\omega = \gamma H_0$ is applied, the spin system will absorb energy from the oscillating field. The sharpness $\Delta \omega$ of this resonant
absorption is inversely proportional to another characteristic time, the spin-spin relaxation time \( T_2 \). This relaxation time \( T_2 \) is a measure of the time that it takes to bring the spins into equilibrium with each other.

In the major part of this study, the proton \( T_1 \) is investigated. So now let's turn to a discussion of how spin-lattice relaxation takes place. A spin in a high energy state can make a transition to a low energy state by either spontaneous emission or stimulated emission. The probability of spontaneous emission is proportional to the third power of the frequency of the oscillating field\(^a\). For protons at 40 MHz, it is \( 2\gamma^2 \omega^3 \hbar^2 / 3c^3 \cdot 10^{-23} \text{sec}^{-1} \), which is very small indeed. Since nuclear \( T_1 \)'s are many orders of magnitude faster than this, it is apparent that the dominant NMR transitions are stimulated. Stimulated emission occurs when the spin experiences magnetic or electric fields fluctuating at its Larmor frequency. A number of interactions between the spin system and the lattice have been found to be important in producing such fluctuating fields. A few examples are:

1. Magnetic dipole-dipole relaxation, in which the source of the fluctuating magnetic field is another nuclear magnetic moment.

2. Paramagnetic relaxation. Since an unpaired electron has a magnetic moment three orders of magnitude larger than that of a proton, it is an effective source of the randomly
fluctuating magnetic field.

(3) Quadrupolar relaxation. If the nucleus has an electric quadrupole moment, a randomly varying electric field gradient (EFG) can interact with it. Since throughout this study protons with spin I = 1/2 are investigated, this mechanism is not relevant. In general, any interaction which gives rise to fluctuating fields at a nucleus is a possible relaxation mechanism.

B. Spin-lattice Relaxation Mechanisms

Various spin-lattice relaxation mechanisms are discussed in detail in several well-known texts. Only those mechanisms important to this study are summarized in the following.

1. Dipolar (Diffusion) contribution

In many cases, the nuclear dipole-dipole interaction is the dominant relaxation mechanism, so we discuss it first and in some detail. Besides, the same relaxation formulism also applies to some other interactions.

The interaction energy between two magnetic moments $\mathbf{\mu}_1 = \gamma_1 \mathbf{\hbar}_1$ and $\mathbf{\mu}_2 = \gamma_2 \mathbf{\hbar}_2$ is

$$W_{12} = \frac{(\gamma_1 \gamma_2 \mu_0^2)}{r_{12}^3}$$

$$\left\{ (\mathbf{\mathbf{r}}_1 \cdot \mathbf{r}_2) - 3 (\mathbf{\mathbf{r}}_1 \cdot \mathbf{\mathbf{r}}_1)(\mathbf{\mathbf{r}}_2 \cdot \mathbf{\mathbf{r}}_2)/(r_{12}^2) \right\}$$

where $r_{12}$ is the separation of the spins, and $\mathbf{r}_1$ and $\mathbf{r}_2$ are
the position vectors. Equation 2-3 can be written as
\[ W_{12} = -\mu_2 \cdot \vec{H}_{12} = -\gamma_2 \vec{H}_{12} \cdot \vec{H}_{12} \]
where \( \vec{H}_{12} \) is called the local field produced by spin 1 at the site of spin 2. The strength of the interaction depends on the magnetic moments of the two spins, the separation of the spins, and their relative orientation. If the spins move about in space, the separation and position vectors of the spins will be functions of time, and the interaction energy becomes time dependent. In other words, atomic diffusion will create a time varying local field. The Fourier component of this fluctuating magnetic field at the spin's Larmor frequency will be effective in causing spin transitions to occur.

In order to express the relaxation rate quantitatively, it is necessary to introduce two closely related functions, namely a correlation function \( G(\tau) \) and its Fourier transform \( J(\omega) \), the spectral density function. Let \( F(t) \) be a component of the randomly time varying local field at time \( t \), and \( F(t+\tau) \) be that at some later time \( t+\tau \). The correlation function is defined by
\[ G(\tau) = F(t)F^*(t+\tau) \] (2-4)
where \( F^* \) is the complex conjugate of \( F \), and the bar over the \( F \)'s indicates an ensemble average. The function \( G(\tau) \) tells us how \( F \) at one time is correlated to its value at a later time. It is independent of \( t \) if \( F \) is a stationary random function of time (i.e., invariant under a change of the origin of time).
The Fourier transform of \( G(\tau) \) or the spectral density is then given by
\[
J(\omega) = \int_{-\infty}^{\infty} G(\tau) \exp(-i\omega \tau) \, d\tau. \tag{2-5}
\]

The spin-lattice relaxation rate can be derived through the time-dependent perturbation theory as was done by Bloembergen, Purcell and Pound\textsuperscript{33} or by the use of the density matrix approach\textsuperscript{34} which turns out to be equivalent. In the presence of a strong Zeeman field the dipolar interaction can be treated as a time-dependent perturbation term. Therefore the Hamiltonian consists of a large time-independent interaction \( \mathscr{H}_0 \) and a smaller but time-dependent term \( \mathscr{H}_1(\tau) \).

For two spins I and S the dipolar interaction can be expressed as\textsuperscript{30}
\[
\mathscr{H}_1 = \sum_{q} F^{(q)} A^{(q)} \tag{2-6}
\]
where \( q = 2, 1, 0, -1, -2 \), corresponding to the Zeeman quantum-number changes. The \( F^{(q)} \) are random functions of the relative positions of the two spins, and the \( A^{(q)} \) are spin-operator terms with the properties
\[
F^{(q)} = F^{(-q)*}; \quad A^{(q)} = A^{(-q)*}.
\]
For simplicity we assume that each component of \( F^{(q)} \) fluctuates independently, so that \( F^{(q)}(t)F^{(q')*}(t+\tau) = \delta_{qq'} \) for \( G^{(q)}(\tau) \).

When each spin I interacts with several identical spins, the correlation function is given by\textsuperscript{35}
\[
G^{(q)}(\tau) = \sum_{j} F_{ij}^{(q)}(t)F_{ij}^{(q)*}(t+\tau) \tag{2-7}
\]
where the summation $\sum_j$ is over all surrounding spins from the typical spin labeled $i$, and

$$F_{ij}(q)(t) = \frac{d_q Y_{2,q}(Q_{ij})}{r_{ij}^3}$$

(2-8)

with $d_q^2 = 16\pi/5$, $d_i^2 = 8\pi/15$, and $d_j^2 = 32\pi/15$.

In the above equation, $Y_{2,q}$ are normalized spherical harmonics and the coordinates $(r,\theta,\phi)_{ij}$ which describe the relative positions of two spins labeled $i$ and $j$ are time dependent due to diffusion of the spins.

As already mentioned, the spectral density function $J^{(q)}(\omega)$ is related to the correlation function by a Fourier transformation. Therefore we have

$$J^{(q)}(\omega) = \int_0^\infty G^{(q)}(\tau) \exp(-i\omega\tau) \, d\tau$$

(2-9)

and the inverse relation

$$G^{(q)}(\tau) = \frac{1}{2\pi} \int_0^\infty J^{(q)}(\omega) \exp(i\omega\tau) \, d\omega.$$  

(2-10)

The relaxation rate $T_{1d}^{-1}$ is expressed in terms of the spectral density function $J^{(q)}(\omega)$. It can be shown that

$$T_{1d}^{-1} = \frac{3}{2} \gamma^4 \mu^2 I(I+1) \left[ J^{(1)}(\omega_{bc}) + J^{(2)}(2\omega_{bc}) \right]$$

(2-11)

where $\omega_{bc}$ is the Larmor frequency of the spin $I$. Here we see that $T_{1d}^{-1}$ depends not only on the strength of the coupling between the spins but also on the values of $J^{(1)}(\omega_{bc})$ and $J^{(2)}(2\omega_{bc})$.

As we observed in Equation 2-9, the form of $J(\omega)$ is determined by the correlation function of the local field fluctuations. The "average" time between the field fluctuations is called the correlation time $\tau_c$. Since $J(\omega)$ is
the spectral density of $G(\tau)$, we expect that $J(\omega)$ will be more
or less uniform for $\omega < 1/\tau_c$ and fall down to zero for $\omega > 1/\tau_c$.
By looking at the dependence of $J(\omega)$ on $\omega$ we can get a little
more insight into the relation between $T_{1d}^{-1}$ and $\tau_c$.

First of all, it is important to note from Equation 2-10
that

$$G(0) = (1/2\pi) \int_{-\infty}^{\infty} J(\omega) \, d\omega$$

(2-12)
is independent of $\tau_c$. It tells us that the area under the
spectral density curve, which corresponds to the power
available in the relaxation spectrum, is fixed as $\tau_c$ varies.
$\tau_c$ only changes the shape of $J(\omega)$. A set of curves of $J(\omega)$
for four different $\tau_c$'s is shown in Figure 2.1. If $\tau_c$ is
long, there is no power available for the transition at Larmor
frequency. If $\tau_c$ is short, the power spectrum is distributed
over a very wide frequency range but its intensity is small.
In either case $T_{1d}^{-1}$ will be small. For an intermediate value,
of $\tau_c - 1/\omega_c$, $J(\omega_c)$ is maximum and $T_{1d}^{-1}$ will be largest.

In metal-hydrogen systems the proton is localized at a
specific interstitial site. A diffusive processs to another
site requires thermal activation. The model used for the
usual calculations assumes that the actual change in the
proton state takes place very quickly, and that the proton
then stays in that state for a time $\tau_0$, the mean dwell time,
until the next jump occurs. The temperature dependence of $\tau_0$
may be expressed in the usual form
Figure 2.1  Schematic representation of $J(\omega)$ for four values of correlation time, illustrating the variations that keep the area under the curves constant as $\tau_c$ changes. $J(\omega)$ is a maximum for the curve of medium $\tau_c$. 

$T_1 < T_2 < T_3 < T_4$ 

$J(\omega)$ 

$\omega$ 

$\omega_0$
\[ \tau_0 = \tau_{00} \exp\left[\frac{E_a}{(k_B T)}\right] \]  

(2-13)

where \( E_a \) is the activation energy, \( k_B \) is Boltzmann's constant, \( \tau_{00} \) is a constant prefactor related to the reciprocal of the jump attempt frequency, and \( T \) is the absolute temperature.

The correlation time \( \tau_c = \tau_0 / 2 \) for proton-proton interactions, and \( \tau_c = \tau_0 \) for proton-metal interactions. As implied earlier, a graph of \( T_1^{-1} \) versus \( T \) will have a maximum at some temperature where the spectral density contribution at the Larmor frequency is a maximum.

The calculation of the exact spectral density for any real atomic motion is difficult because the atomic motions are extremely complicated. A simple form of \( J^{(q)}(\omega) \) was suggested by Bloembergen, Purcell and Pound\(^3\)\(^4\) (referred to as BPP). It is assumed that

\[ G^{(q)}(\tau) = G^{(q)}(0) \exp\left(-|\tau|/\tau_c\right) \]  

(2-14)

where \( \tau_c \) is the correlation time.

Then the spectral density at frequency \( \omega \) becomes

\[ J^{(q)}(\omega) = G^{(q)}(0) \left[\frac{2\tau_c}{(1+\omega^2 \tau_c^2)}\right]. \]  

(2-15)

Although the Lorentzian form for \( J(\omega) \) in Equation 2-15 occurs\(^3\)\(^4\) only when a local field changes sign with a frequency of \( 1/\tau_c \), we consider that it is sufficient to use this model in the analysis of our results, since an atomic jump represents an abrupt change in the local field.
2. Conduction-electron contribution

In metals the hyperfine coupling between electronic and nuclear spins is also a significant mechanism for nuclear spin-relaxation\textsuperscript{3,6}. Korringa\textsuperscript{3,7} pointed out that the dominant contribution to nuclear relaxation comes from the scalar contact coupling between the nuclear and electronic spins. The Hamiltonian can be written as

\[ H = -\frac{8\pi}{3} \gamma_e \gamma_n \mathbf{H} \cdot \mathbf{r} \cdot \mathbf{s} (\mathbf{r}) \]  \hspace{1cm} (2-16)

where \( \mathbf{r} \) represents the vector connecting electron and nuclear spins, \( \mathbf{s}, \mathbf{i}, \) and \( \gamma_e, \gamma_n \) are the angular momentum and gyromagnetic ratio of the electron and nuclear spin, respectively. This interaction can induce a simultaneous flip of the electron and nuclear spins in opposite directions.

During a nuclear transition, a simultaneous electron transition from some state of wave vector \( \mathbf{k} \) and spin orientation \( \mathbf{s} \), to a state \( \mathbf{k}', \mathbf{s}' \) occurs. The energy required for such a mutual spin flip is provided by the change in the kinetic energy of the electron. Because of the Pauli principle only electrons close to the Fermi level are able to participate in the process.

It has been shown that\textsuperscript{3,4,38} the spin-lattice relaxation of a nuclear spin system by conduction electrons can be described by the change of spin temperature of the spin system. Then one can get an important relation between the relaxation time \( T_{1e} \) and the Knight shift \( \Delta H/H_0 \),
\[ T_{ie} \left( \Delta H/H_0 \right)^2 = \left( \frac{\hbar}{4\pi n k_B T} \right) \frac{\gamma_e}{\gamma_n} \left( \frac{\chi_n}{\chi_o} \right)^2 \left[ \frac{N_o (E_F)}{N_s (E_F)} \right]^2 \]  \hfill (2-17)

where \( \chi \) and \( N \) are the susceptibility and the density of states of the electrons, respectively, and subscript "o" refers to the independent electron approximation. This equation is called the "Korringa relation".

In transition metals, the electrons at the Fermi Level occupy both s and d orbitals. A partitioned model which neglects the mixing of the s and d bands and the electron-electron correlation gives

\[ \frac{1}{T_{ie}} = 4\pi n \gamma_n^2 k_B T \left\{ H_{hf}^{(s)} N_s (E_F) \right\}^2 + \left\{ H_{hf}^{(d)} N_d (E_F) \right\}^2 q + \left[ H_{hf}^{(o)} N_d (E_F) \right]^2 p \] \hfill (2-18)

where \( N_s (E_F) \) and \( N_d (E_F) \) are the s-band and d-band density of states at the Fermi level, respectively; \( H_{hf}^{(s)} \), \( H_{hf}^{(d)} \) and \( H_{hf}^{(o)} \) are the hyperfine fields at the resonant nucleus caused by the contact interaction with the unpaired s electrons, the core polarization by the unpaired d electrons, and the orbital motion of the d electrons, respectively. The quantities \( p \) and \( q \) are the band reduction factors related to the d-electron orbital degeneracy at \( E_F \). Since \( N_d (E_F) \) is usually much larger than \( N_s (E_F) \), \( T_{ie} \) is dominated by the core polarization and the orbital terms. The quantities in \( [] \) in Equation 2-18 are essentially temperature-independent if \( E_F \) does not lie on a sharp peak in the density of states, and thus \( T_{ie} \) obeys

\[ T_{ie} \propto \frac{1}{T} = \text{constant}. \] \hfill (2-19)
The constant in Equation 2-19 can give useful information on the density of states, but the quantitative character is not readily established because several parameters in Equation 2-18 cannot be easily evaluated.

3. Paramagnetic ion contribution

As early as 1949, Bloembergen has already shown that nuclear spin relaxation in insulating solids at low temperatures can be due to small amounts of paramagnetic impurity ions. In a recent investigation by Phua et al., the Gd\(^{3+}\) ion in yttrium and lanthanum dihydrides was shown to be very effective in promoting proton spin-lattice relaxation at both low and high temperatures.

In general, the protons are coupled to the paramagnetic ions both by dipolar interaction and indirect interaction through the conduction electrons (the RKKY interaction). However in the work by Phua et al. for the case of Gd\(^{3+}\) impurity in YH\(_2\) and LaH\(_2\), it was found that the RKKY interaction is too small to account for the relaxation. It is the magnetic dipolar interaction that dominates in the paramagnetic ion contribution, at least in the case of Gd\(^{3+}\) impurities.

We first assume that the temperature is so low that atomic diffusion can be ignored (the rigid lattice regime). For a nucleus at a distance r from the ion the nuclear
relaxation rate $1/\tau(r,\theta)$ due to direct dipolar interaction is

$$\frac{1}{\tau(r,\theta)} = \left[ \frac{3}{2n} \right] (\gamma_n \gamma_p M)^2 J(J+1) r^{-6} \sin^2 \theta \cos^2 \theta$$

$$\times \left[ \frac{(2n \gamma_n^2)}{1+\omega^2 \tau^2} \right]$$

(2-20)

where $\theta$ is the polar angle of the vector joining the nucleus and the impurity ion relative to the applied field, $\omega_0$ is the Larmor frequency of the nucleus, $\gamma_n$ is the gyromagnetic ratio of the nucleus, $J$, $\gamma_p$, and $\tau_1$ are the angular momentum, gyromagnetic ratio, and spin-lattice relaxation time of the impurity ion, respectively. This process induces a flip of the nuclear spin unaccompanied by an impurity ion flip.

For a powder sample, we eliminate the angular dependence in Equation 2-20 by averaging over the angle $\theta$, and get

$$\tau^{-1}(r) = \left( \frac{2}{5} \right) (\gamma_p \gamma_n M)^2 J(J+1) r^{-6} \left[ (\tau_1)/(1+\omega^2 \tau^2) \right]$$

$$= C r^{-6}$$

(2-21)

where $C$ is a measure of the interaction strength between the nucleus and the ion, and is defined by

$$C = \left( \frac{2}{5} \right) (\gamma_p \gamma_n M)^2 J(J+1) \left[ (\tau_1)/(1+\omega^2 \tau^2) \right]$$

(2-22)

We consider the case of very dilute impurity concentration in which each nuclear spin is affected by only one impurity ion. Due to the inverse sixth power dependence on distance in Equation 2-21, only those nuclei close to the impurity are relaxed by direct interaction. Spins far from the impurity ion have to interact with the ion indirectly by
the mechanism of spin diffusion, which occurs through the mutual flips between neighboring spins. In this process, nuclear magnetization diffuses among the spins to the impurity ion. It is not the actual diffusion of the nucleus itself but just of its polarization. The rate at which the magnetization is transported is characterized by the spin diffusion coefficient $D_s$. Bloembergen\textsuperscript{40} first made an estimate of the spin diffusion coefficient for a simple cubic lattice. He obtained

$$D_s = a^2/(50T_2)$$ \hspace{1cm} (2-23)

where $a$ is the internuclear spacing and $T_2$ is the rigid-lattice spin-spin relaxation time.

Lowe and Gade\textsuperscript{41} derived a spin diffusion equation for spin-$1/2$ nuclei and found $D_s$ in the simple cubic lattice,

$$D_s = 0.15\gamma^2\mu/\alpha$$ \hspace{1cm} (2-24)

where $\gamma$ and $\alpha$ are gyromagnetic ratio and nearest-neighbor spacing of the spins, respectively. This expression gives values about 2 times larger than Bloembergen's values.

After Bloembergen, the theory of nuclear relaxation by diffusion to paramagnetic impurities was developed further by several workers: de Gennes\textsuperscript{42}, Blumberg\textsuperscript{43}, Rorschach\textsuperscript{44}, etc. The nuclear spin-lattice relaxation rate for the average macroscopic magnetization is governed not only by the direct relaxation rate but also by the rate due to spin diffusion. Thus, two limiting cases arise in the relaxation process:
slow diffusion limit and fast diffusion limit.

In the slow diffusion limit, the relaxation process is controlled by the rate at which spins can diffuse to the impurity ion. Khutsishvili and de Gennes calculated the relaxation rate in this limit. The expression is

$$R_{ip} = \frac{8\pi}{3} N D_s \beta$$ (2-25)

where $N$ is the impurity concentration per unit volume, and $\beta$ is called the pseudopotential radius defined by

$$\beta = (C/D_s)^{1/4}.$$ (2-26)

The pseudopotential radius $\beta$ is essentially the distance from the ion at which the direct relaxation rate in Equation 2-21 equals the spin diffusion rate $-D_s/r^2$.

In the fast diffusion limit, the relaxation process is controlled by the rate at which the impurity ion can relax its neighboring spins. Blumberg obtained

$$R_{ip} = \frac{4\pi}{3}(NC/b^2)$$ (2-27)

in this limit. A length parameter $b$, usually called the barrier radius, is introduced in Equation 2-27. Diffusion of magnetization to the region inside the barrier radius cannot occur because, due to the local field of the impurity ion, the Larmor frequencies of adjacent spins are sufficiently different so as to prevent an energy-conserving mutual spin flip.

Rorschach has taken the influence of the barrier radius on relaxation rate into account and obtained a general
expression for $R_{tp}$ valid in all cases:

$$R_{tp} = 8\pi N D_a \beta \left[ \frac{\Gamma(3/4)}{\Gamma(1/4)} \right] \left[ \frac{I_{3/4}(\delta)}{I_{-3/4}(\delta)} \right]$$  \hspace{1cm} (2-28)

where $I_m(x) = i^{-m} J_m(ix)$ is the modified Bessel Function\(^6\), $\delta = \beta^2/(2b^2)$, and $\Gamma$ is the gamma function. The value of $\delta$ determines the two limiting cases mentioned earlier. For $\delta \geq 2$, $I_m(\delta) \equiv I_{-m}(\delta)$ and Equation 2-28 reduces to

$$R_{tp} \equiv \frac{8\pi}{3} N D_a \beta = \frac{8\pi}{3} N C^{1/4} D_a^{3/4}$$  \hspace{1cm} (2-25')

in agreement with Equation 2-25 for the slow diffusion limit.

For $\delta < 0.3$, $I_m(\delta) \rightarrow [1/\Gamma(m+1)](\delta/2)^m$ and Equation 2-28 yields

$$R_{tp} \equiv \frac{8\pi}{3} N D_a \beta \left[ \frac{\beta^3/(2b^3)}{} \right] = \frac{4\pi}{3} (\frac{NC}{b^3})$$  \hspace{1cm} (2-27')

as in Equation 2-27 for the fast diffusion limit.

Following the formulation of Rorschach\(^4\), the barrier radius $b$ is a function of the average moment of the impurity ion $\langle \mu_p \rangle$ and is given by

$$b = \left( \frac{3\langle \mu_p \rangle}{\mu_n} \right)^{1/4} a$$  \hspace{1cm} (2-29)

where $\mu_n$ is the nuclear moment and $a$ is the internuclear spacing. The effective static component of the ion moment $\langle \mu_p \rangle$ is given by

$$\langle \mu_p \rangle = \wp \mathcal{H} [B^2(x) + (\partial B/\partial x)(2/\pi) \tan^{-1} \left[ \frac{2\pi \gamma_1}{T_2} \right]]^{1/2}$$  \hspace{1cm} (2-30)

where $B(x)$ is the Brillouin function in which $x = \wp \mathcal{H}/(k_b T)$, and $H_o$ is the applied field.

The expressions for $R_{tp}$ discussed above can be extended to the higher temperature range where atomic diffusion becomes significant. Shen\(^7\) first suggested that in the higher temperature range where the atomic diffusion coefficient $D_a >$
Da, Da can be replaced by Da. He proposed an expression for the slow atomic diffusion limit,

\[ R_{1p} = \frac{(8\pi/3)NDa\beta'}{(8\pi/3)NC^{1/4}Da^{3/4}} \]

with \( Da = D_0 \exp[-E_a/(k_BT)] \)

and \( \beta' = (C/DA)^{1/4} \).

Richards\textsuperscript{48} extended Rorschach's general expression, Equation 2-28, to the temperature range where \( Da \gg Da \), and obtained

\[ R_{1p} = \frac{8nNDa\beta'\Gamma (3/4)/\Gamma (1/4)}{[\Gamma (3/4)/(\delta_a)/(\Gamma - 3/4)(\delta_a)]} \]

with \( \delta_a = (\beta')^2/(2a_1^2) \).

In the above equation the barrier radius \( b \) has been replaced by \( a_1 \), the distance of closest approach of a nucleus to the impurity ion, and the correlation time for the interaction now becomes

\[ \tau_{l_{1-1}^* - 1} = \tau_{l_{1-1}} + \tau_{0-1} \].

Just as in the spin-diffusion case, there is a fast atomic diffusion form, which is obtained from Equation 2-27 by replacement of \( D_s \) by \( Da \), \( \beta \) by \( \beta' \), and \( b \) by \( a_1 \):

\[ R_{1p} = (4\pi/3)(NC/a_1^3) \]

This limit is appropriate to temperatures sufficiently high that \( \tau_0 \ll \tau(a_1) \).

Some samples used in this study were doped with controlled levels of gadolinium. Since the proton \( R_{1p} \) depends on the Gd\textsuperscript{3+} ion relaxation time \( \tau_1 \), which in turn is sensitive to the electronic properties of the samples, knowledge of \( R_{1p} \).
enables the electronic properties of the samples to be studied by way of the temperature dependence of $\tau_1$. In the last part of this section spin-lattice relaxation of rare-earth ions in crystals will be mentioned briefly.

4. Spin-lattice relaxation of rare-earth ions in crystals

In ionic crystals a spin system can pass its energy to the crystal lattice through the coupling of the spins with the thermal vibrations of the lattice. It has been shown by Van Vleck that the dominant spin-lattice interaction is through the thermal modulation of the Stark field. When the lattice vibrates, the orbital motion changes due to variations of the crystalline electric fields (CEF). These changes react on the spins through the spin-orbit coupling. Two principal mechanisms are important. The simplest mechanism is a one-phonon direct process in which a phonon is absorbed or emitted, accompanied by a spin-relaxation transition. Another mechanism is a two-phonon Raman process in which a phonon is scattered by a spin and another phonon with different energy is emitted accompanied by a spin-relaxation transition. Ordinarily the direct process predominates at low temperatures.

The theory of rare-earth-ion relaxation has been developed by Orbach, who used a simple orbit-lattice interaction to estimate the spin-lattice relaxation time. It
is found that for Kramers ions cerium, neodymium, dysprosium, erbium, and ytterbium, the direct process relaxation time is characterized by a $1/T$ temperature dependence, i.e., $\tau_i \propto 1/T$, while the Raman process depends on temperature as $\tau_i \propto T^{-9}$.

Since the $S$-state ions gadolinium $\text{Gd}^{3+}$ and europium $\text{Eu}^{2+}$ are not perturbed by a crystal field in first order, the crystalline field splittings and the relaxation rate are usually small. In such small crystal-field splittings, any spin-orbit state can be considered as a multilevel state. Orbach and Blume showed that in such multilevel systems the spin-lattice relaxation time due to the two-phonon Raman process is proportional to $T^{-5}$, i.e.,

$$\tau_i \propto T^{-5}. \quad (2-38)$$

The behavior of paramagnetic ions in metals is similar to that of nuclear spins in metals in many aspects. It is usually assumed that for $S$-state ions an exchange-type Hamiltonian can phenomenologically describe the coupling between the magnetic ion and the conduction electron,

$$H = -\frac{1}{n_0} \sum_{\sigma} J \hat{S}_n \cdot \hat{\sigma}(\vec{r}) \delta(\vec{R}_n - \vec{r}) \quad (2-39)$$

where $\hat{S}$ is the ionic spin, $\hat{\sigma}(\vec{r})$ is the electronic spin density, $J$ is an exchange interaction parameter with the dimension of energy, $\vec{R}_n$ are the lattice sites occupied by the ions, and $n_0$ is the number of lattice sites per unit volume. Since Equation 2-39 is similar to the contact Hamiltonian for the nuclear spin system in metals (Equation 2-16), one would
expect an ion spin-lattice relaxation to be analogous to the Korringa relaxation. Measurements of the linewidth of the Gd$^3^+$ ESR in lanthanum dihydrides show that the linewidths increase linearly with increasing temperature which is thought to originate mostly from the spin-lattice relaxation due mainly to a Korringa-type relaxation, $\tau_1 \propto T^{-1}$, via conduction electrons.
III. EXPERIMENT ASPECTS

A. The NMR Pulsed Spectrometer

Relaxation time measurements were made using a phase-coherent NMR pulsed spectrometer. It was constructed by Adduci, Hornung, and Torgeson in the Ames Laboratory. A block diagram of the spectrometer is shown in Figure 3-1. Basically the spectrometer consists of the following units: magnet, pulse programmer, transmitter, probe, receiver, signal averager, and temperature control.

1. Magnet

Two magnets were employed. For the measurements at temperatures above 140 K, the static magnetic field was supplied by a Varian Associates model V-4012A magnet. The field was set to the value of 9395 G for the proton resonance at 40 MHz. The stability of the field was satisfactory. However, a deuteron NMR field stabilizer was used to prevent residual field drift, which became significant in the temperature range where motional narrowing took place. The liquid sample used in the field stabilizer was D₂O to which MnSO₄·H₂O at a concentration of 0.25 moles/liter D₂O was added. The field then locked at the ²D resonance frequency of 6.1402 MHz which corresponds to the proton resonance frequency of 40 MHz in the same field.
Figure 3.1 The block diagram of the pulsed NMR spectrometer used in this work. The heavy lines indicate the path of the NMR signal.
For the measurements below 140 K, a Magnion nine-inch magnet was used, model L-96, with a three-inch gap spacing, powered by an HS-1365B current regulated supply. Another NMR field stabilizer tuned to the $^2$D resonance frequency was used to stabilize this magnet.

2. Pulse programmer

The pulse programmer used in the spectrometer was built in the Ames Lab and is a modification of the Conway-Cotts design. It created the pulse trains and triggers for the measurements. Each pulse sequence can repeat at a fixed rate set by a clock module which has digitally selectable rates ranging from 1μs to 999 s. Three channel modules exist in the programmer. Each of the channel modules produces from one to 999 pulses, having the same pulse length and phase, with selected intervals between them. The length of each pulse is set by an analog control which is continuously adjustable. A time delayed trigger pulse follows each pulse to start external equipment. Also there is a delayed start pulse following each channel pulse to start the next channel. The time base of each channel is set independently of either the clock or other channels. An auto-increment module in the programmer will automatically advance the time spacings between groups of pulses. This is particularly useful in spin-lattice relaxation time measurements as will be described
later. The automatic time incrementing can be set with 1, 2, 4, or 8 times the selected time base, ranging from 0.1μs to 1 s.

3. Radiofrequency transmitter

The radiofrequency (rf) transmitter has its 40 MHz frequency source in a crystal controlled continuous wave oscillator which also provides the 10 MHz time base for the programmer. The rf output is amplified and split into three independently adjustable paths in the rf switching module. Two of these paths provide two possible phases to the transmitter, and the remaining one goes to the phase sensitive detector. The output logic pulses from each channel module in the programmer were delivered to the rf switch module in which the phase of the rf pulse is selected. The rf switch has a variable rf amplitude path A and a variable rf phase path B. An important requirement for the phase sensitive detection and the stability of multiple pulse measurements is that all pulses be coherent to each other (definitely related in phase). This requirement can be achieved in the rf switch module in which the rf is switched to the selected path and switched again simultaneously at the summing point, thereby doubly isolating the cw source rf from the transmitter. The rf pulses output to the sample coil are amplified by an Arenburg Ultrasonics model PG-650C gated amplifier at a power
level of approximately 800 watts. This transmitter is capable of producing rf pulses with $H_0 = 30$ G which is strong enough to carry out the pulsed NMR measurements.

4. The sample probe

The sample probe which consists of a sample coil and a matching system is of special importance to the performance of the spectrometer. It is designed for the efficient transfer of rf energy from the transmitter to the coil and from the coil to the receiver. A good probe system should meet the following requirements. First, the input impedance $Z_{in}$ which it presents to the transmitter and to the receiver should be purely resistive. Second, it should produce a large, homogeneous rf field $H_i$ over the sample. Third, it should tune to the resonance frequency, and the tuning must be done to maximize the power in the $H_i$ field and minimize the ring-down of the system. The quality factor Q gives the ratio of stored energy to the dissipated energy per cycle in the probe. Although an increase in Q value will improve the signal to noise ratio, it will lengthen the ring-down time as well. Because a single-coil is used for both transmission and reception, a long ring-down time means a long receiver dead-time which prevents the detection of the nuclear signal. The Q value can be chosen only as a compromise. Finally, the probe must fit in the pole gap of the magnet and also
withstand the highest operating temperature.

Two probes were used in this study: a standard probe which operates for temperatures between 140 K and 700 K, and a low temperature probe which operates from room temperature down to liquid helium temperature. Both probes have similar structures in sample coil and matching system. The only difference is in their temperature chambers. Figure 3-2 shows the diagram of the probe circuits. The coil L is a homemade simple solenoid. It was made of No. 15 copper wire with its nyl clad insulation burned off. The coil was 35 mm long, had 15 turns and an inner diameter to accommodate 10 mm quartz tubes containing the samples. C₁ and C₂ are variable capacitors. The values of L and C determine the resonant frequency. The resistor R determines Q (= ωL/R) and the ring-down time. The probe was tuned by adjusting the two capacitors with a Hewlett Packard 4815A RF vector impedance meter. Q was determined with a sweep generator and a 10db directional coupler. From the bandwidth at half-height, Q is given by Q = ν₀/Δν.

The performance of the probe was satisfactory. Q was about 40, the length of the 90° pulse for protons was ~3μs, and the dead-time of the probe plus receiver was ~10μs.

5. Receiver

The receiver consists of a series of three Spectrum Microwave wideband Limiting Amplifiers, model SML-D. They are
TAPPED PARALLEL TUNED \( (f_0 \leq 20 \text{ MHz}) \)

\[ \begin{array}{c}
\text{C2} \\
50 \text{ Ohm} \\
\text{C1} \\
\end{array} \]

TAPPED SERIES TUNED \( (f_0 \geq 20 \text{ MHz}) \)

\[ \begin{array}{c}
\text{C1} \\
50 \text{ Ohm} \\
\text{C2} \\
\end{array} \]

Figure 3.2 RF matching circuits
connected by low Q series filters tuned at the operating frequency. The recovery time to full operating gain is about 400 ns. In the rf portion the signal gain is about 60 db. The signal at the end of the rf chain is phase sensitively detected with a reference signal from the rf switch module. Then the video signal is amplified further by an operational amplifier-filter combination which has an unfiltered bandwidth of 1 MHz and selectable filter and gain level. The gain bandwidth product is about 50 MHz with gain selectable 30, 35, 40, 45, and 50 db. The signal is then fed to a Biomation 805 waveform recorder or displayed on an oscilloscope.

Next, let's consider the circuit connecting the probe to the transmitter and receiver. Ideally the probe should be connected to the transmitter and disconnected from the receiver when the transmitter is on, while during signal reception the probe should be connected to the receiver and disconnected from the transmitter. The switching circuit (or duplexer circuit) used is shown in Figure 3-1. It is similar to Lowe and Tarr's design. This switching uses the properties of diodes and the length of the coaxial cable. The diode conducts only whenever the voltage across it exceeds about 0.5 V. Therefore, a pair of crossed-diodes acts as a voltage activated switch, which is independent of frequency. The behavior of the coaxial cable depends on its length and characteristic impedance and is strongly frequency dependent.
A one-quarter wavelength cable can be used as an impedance transformer to transform a short circuit into an open circuit or vice-versa.

As shown in Figure 3-1, four one-quarter wavelength cables, two series-diodes and two diode-shorts were employed. During the transmission mode, the crossed-diode switches are conducting. The conducting series-diodes connect the transmitter with the probe which is tuned to the characteristic impedance at operating frequency. On the other hand, the conducting diode-short following the one-quarter wavelength cable is transformed to a high impedance so that almost no rf energy can propagate. The next one-quarter wavelength cable and diode-short reduce the rf energy going to the receiver further. Thus the receiver is disconnected. During the receiving mode, the diode switches do not conduct and hence the probe is disconnected from the transmitter. But now the high resistance of the diode-short is in parallel with the 50Ω impedance of the receiver so that the probe sees the one-quarter wavelength cable as a 50Ω load. Consequently, the probe and receiver are connected and matched.

6. Data averaging and storage

Averaging of the detected signals was done using a Biomation 805 transient recorder interfaced to a Nicolet 535 signal averager. Both were operated in the external address
advance mode. The address advance pulses were sent out by the pulse programmer so that the data curve of signal amplitude versus time could be obtained. Signals sampled at a fixed location of the free induction decay were transferred from the Biomation transient recorder to the Nicolet signal averager and stored in its memory after the external advance trigger pulse was sent. This process was repeated until the averager reached its pre-set count for the data points. Multiple accumulations could be performed by using a trigger to reset the channel address. By so doing the signal to noise ratios were improved because of the averaging effect on the noise.

An interface built by the Ames Lab Instrumentation Group was used to transfer the data from the Nicolet signal averager to a Digital Equipment Corporation LSI-11 computer. Then the data was fit using a least squares fit program. The data and the least squares fit were also transferred back to the Nicolet for inspection. All this information could be stored on floppy disk by the LSI-11 computer or read out from an oscilloscope or on the chart recorder.

7. Temperature control

As mentioned earlier, two sample probes were used to cover the temperature range in this study. Their sample chambers are different.
a. Standard probe

The standard probe has a cylindrical counter-flow nitrogen gas-blowing chamber, designed and built by D. R. Torgeson in the Ames Laboratory. This gas-flow chamber operates in a temperature range between 100 K and 800 K. Figure 3-3 shows the structure of the sample chamber. The vacuum in the brass jacket serves to insulate the components and reduce the temperature gradient inside the chamber. The heater has a resistance of about 15Ω. The insulated heater wire was first folded at its midpoint and then wound on the cylindrical brass inner-tube to avoid induction. A layer of Sauereisen Electrotemp cement was coated on the surface of the heater coil. Copper-constantan thermocouples were used in the temperature range of 100-666 K. A thermocouple inserted close to the sample was used to monitor the sample temperature and was connected to a Leeds and Northrup type K-3 potentiometer, with the reference temperature maintained at 273.2 K. A Fluke 845AB high impedance voltmeter-null detector was used to monitor the potentiometer balance and gave feedback to the heater power supply. Due to the temperature gradient around the sample area, it was necessary to calibrate the system by inserting a second thermocouple inside a sample tube in the rf coil.

For temperatures above room temperature, a small flow of dry nitrogen gas was heated by the heater and then passed across the sample. The temperature was maintained by the
Figure 3.3 The gas-flow chamber used for temperatures between 100 K and 800 K.
current from the heater power supply and regulated by the feedback regulation system. For temperatures below room temperature, cold nitrogen gas supplied by controlled boiling of liquid nitrogen (using two 66Ω, 150 W heaters in a 50-liter storage dewar) was led into the chamber. The temperature was maintained by the flow rate of the cold nitrogen and the heater inside the chamber which was again regulated by the feedback system.

b. Low-temperature probe An Air Products HELI-TRAN cryostat with a metal probe dewar built by L. Lichty was employed. Because the dewar is made of metal, helium flow through the dewar can be controlled by regulating the flow of helium gas leaving the dewar. The temperature was read and controlled by two thermocouples (Au-0.07at%Fe vs. Chromel). A sample thermocouple was inserted in contact with the sample, while a regulating thermocouple and heater were connected to the current-feedback temperature controller. The reference junctions of both thermocouples were maintained at liquid nitrogen temperature. When the sample reached the desired temperature, the sample thermocouple was moved up away from the sample. During actual data taking, the sample temperature was regulated by the regulating thermocouple and the temperature controller.
B. Experimental Methods

The first NMR experiment were the CW (continuous wave) experiments by Bloch, Purcell, and their co-workers. In 1950, Hahn\(^8\) published the first pulsed NMR experiment paper. Pulsed NMR methods make use of pulses of rf power. The nuclear spin system is then observed after the rf is turned off. The time varying signal is usually called the free induction decay (FID). Lowe and Norberg\(^9\) proved that a frequency spectrum in CW NMR is related to the FID in pulsed NMR by Fourier transformation; hence it is possible to obtain the same spectral information from a pulse experiment which is often much more efficient. Further, the pulse techniques provide the most useful method of measuring relaxation times. The proton spin-lattice relaxation time measurements in this work were made with the previously described pulsed NMR spectrometer.

Although many features of NMR spectra can be described only by quantum mechanics based on energy level concepts, most of the pulsed NMR methods are more easily understood through a classical treatment. As already mentioned in Chapter II, in a static magnetic field \(\vec{H}_0\) a spin system gives rise to a macroscopic magnetization \(\vec{M}_0 = \chi_0 \vec{H}_0\) at thermal equilibrium. If the magnetization is somehow disturbed from its equilibrium state it can relax back toward the direction of the field by giving up energy to the surroundings. The motion of the
nuclear magnetization obeys the Larmor relation

\[(d\vec{M}/dt) = \gamma \vec{M} \times \vec{H}_0\]  \hspace{1cm} (3-1)

and precesses about the static magnetic field \(\vec{H}_0\) with an angular velocity \(\omega = -\gamma H_0\).

Pulsed NMR methods deal mainly with the behavior of the magnetization as we disturb it by applying an rf magnetic field, and as it precesses and relaxes towards the equilibrium state in the static field. It is very useful to refer the motion of the magnetization to a coordinate system that rotates about the static field \(\vec{H}_0\) in the same direction in which the magnetization precesses. This coordinate system is usually called the rotating frame.

1. Magnetization in the rotating frame

Let \(S'\) be a frame of reference rotating with angular velocity \(\vec{\omega}\) with respect to the laboratory frame \(S\). According to the general law of relative motion, the time derivative of \(\vec{M}\) in the laboratory frame \(S\) is related to that in the rotating frame \(S'\) by

\[\frac{d\vec{M}}{dt}_S = \frac{d\vec{M}}{dt}_{S'} + \vec{\omega} \times \vec{M}.\]  \hspace{1cm} (3-2)

Combining Equations 3-1 and 3-2, the time derivative of \(\vec{M}\) in the rotating frame \(S'\) is given by

\[\frac{d\vec{M}}{dt}_{S'} = \gamma \vec{M} \times (\vec{H}_0 + \vec{\omega}/\gamma) = \gamma \vec{M} \times \vec{H}_0.\]  \hspace{1cm} (3-3)

This has the same form as Equation 3-1 except that the magnetic field \(\vec{H}_0\) is replaced by an effective field
\[ \hat{H}_e = \hat{H}_o + \hat{w}/\gamma. \]  

(3-4)

If the rotating frame angular velocity \( \hat{w} \) is chosen to be equal to the Larmor velocity \( -\gamma \hat{H}_o \), the effective field \( \hat{H}_e \) vanishes. In the rotating frame, \( (d\hat{M}/dt)_{S'} = 0 \), and the magnetization is stationary. Now suppose that a magnetic field \( \hat{H}_i \) perpendicular to \( \hat{H}_o \) and rotating about it with angular velocity \( \hat{w} \) is applied. We do this by creating a linearly oscillating field with a simple solenoid. In fact, a linearly polarized field \( 2\hat{H}_i \cos \omega t \) is a sum of two fields of amplitude \( \hat{H}_i \), rotating in opposite directions with angular velocities \( \pm \omega \). The rotating frame is fixed to one of these rotating fields, therefore the other rotating field rotates with frequency (in the opposite direction) \( 2\omega \) in the rotating frame and is too high a frequency to affect the magnetization. Let the direction of \( \hat{H}_o \) be the z-axis in the laboratory frame, and of course the z'-axis in the rotating frame. By choosing the x'-axis in the rotating frame to be parallel to \( \hat{H}_i \), the effective field is fixed in the S' frame and is given by

\[ \hat{H}_e = (\hat{H}_o - \omega/\gamma)\hat{k'} + \hat{H}_i \hat{i}'. \]  

(3-5)

In the rotating frame S', the magnetization precesses around the effective field \( \hat{H}_e \) with angular velocity \( -\gamma \hat{H}_e \). Its motion in the laboratory frame is the combination of this with the rotation of S' with respect to S.
2. Spin-lattice relaxation time measurement

In the pulsed NMR experiment, we place the rf coil and sample in the applied static magnetic field. An intense rf pulse in the coil generates a linearly polarized magnetic field $2H_i \cos \omega t$ in the direction parallel to the axis of the coil. The static field is set to meet the resonance condition $H_0 = \omega / \gamma$ so that $\vec{H}_0 = H_1 \hat{z}'$. Equation 3-3 tells us then that in the rotating frame the magnetization $\vec{M}$ which starts out along $z'$-axis precesses about the $x'$-axis with an angular velocity $\gamma H_1$. If the rf pulse is turned on for a time $t_p$ the magnetization vector will be rotated through an angle

$$\theta = \gamma H_1 t_p.$$  

We usually identify pulses as 90°, 180° pulses, etc., by the angles through which the magnetization is turned.

Assume that the rf pulse is sufficiently strong that the length of the pulse $t_p$ is short relative to $T_1$ and $T_2$, i.e., no relaxation occurs during the time $t_p$. (In our experiments pulses of only a few microseconds are used.) Suppose a 90° pulse is applied. Following it, the magnetization lies along the $y'$-axis. This magnetization will precess freely in the $x'y'$-plane and decay in time as the system returns to thermal equilibrium state. This decaying magnetization will then induce a sinusoidal voltage in the coil. Since the coil is perpendicular to the applied field, the strength of the observed signal depends on the magnitude of the magnetization.
in the xy-plane. The signal induced in the coil is called a free induction decay (FID). In a perfectly homogeneous field, the magnetization decays in the x'y'-plane because transverse (spin-spin) relaxation occurs. This process causes the magnetic moments to spread out in the x'y'-plane, thus \( M_{y'} \) decays with a time constant \( T_2 \). Since the magnetic field is not perfectly homogeneous, the nuclei in different parts of the field precess at slightly different frequencies. As the magnetic moments get out of phase with each other, \( M_{y'} \) decays, too. Therefore overall, \( M_{y'} \) decays with time constant \( T_{2*} \),

\[
1/T_{2*} = 1/T_2 + (\gamma \Delta H_0 / 2)
\]

where \( \Delta H_0 \) is the line width due to field inhomogeneity. A phase sensitive detector is referenced in phase to the rf field and it responds to the magnetization which has a fixed phase relative to \( H_1 \). Hence it can distinguish between the magnetization along the + y' and - y' axes.

Spin-lattice relaxation also occurs as \( M_z \) relaxes toward its equilibrium value with time constant \( T_1 \). \( T_1 \) is usually longer than \( T_{2*} \). Because the coil only picks up the signal of the magnetization in the xy-plane, the recovery of \( M_z \) is not detectable unless it is turned away from the z-axis. Therefore we need a second pulse to measure the spin-lattice relaxation time. The procedure used in this experiment is the so called inversion recovery method in which the 180°-τ-90° pulse sequence is utilized to measure \( M_z(\tau) \). In this sequence,
the magnetization $M_0$ is first inverted from the equilibrium $z$-direction to the $-z$ direction by a $180^\circ$ pulse along the $x'$-axis. Due to the spin-lattice relaxation, $M_z$ grows from $-M_0$ to $+M_0$. Then at some time after the $180^\circ$ pulse, a $90^\circ$ pulse is applied, also along the $x'$-axis. This $90^\circ$ pulse rotates $M_z$ into the $xy$-plane so that an FID signal is induced in the rf coil. The initial height of the FID is proportional to the magnitude of $M_z(t)$, the value of $M_z$ at time $t$. After the system has completely returned to equilibrium, the sequence is repeated with a different $\tau$ value. Thus, the growth of the magnetization along the direction of the static field as a function of time can be traced by many repetitions (e.g., 100) of this sequence.

3. Setting up and operating the spectrometer

The probe was tuned to the resonance and matched to the transmitter-receiver system with a Hewlett Packard 4815-A RF vector impedance meter. To maximize the transmitter output to the sample coil, the probe was tuned to 50$\Omega$ and 0$^\circ$ phase by adjusting the two tunable capacitors. The transmitter pulses were maximized for short rise and fall times by tuning the Arenburg gated amplifier. Using an rf signal sampler, the transmitter pulses were displayed on the oscilloscope.

To operate the equipment, several parameters needed to be preset. First, the pulse length corresponding to a $180^\circ$ pulse
on channel 1 was determined by observing the shortest pulse length at which the FID passed through a null. A 90° pulse could be set on channel 2 using two identical pulses and adjusting so that again no FID was observed. Then each single pulse was a 90° pulse. The pulse lengths were measured digitally with the Computer Measurements Co. model 901 counter. Typical 90° pulse length was approximately 3 μsec (corresponding to an rf field strength of 20 G) for the proton resonance at 40 MHz. The position of the sample in the magnetic field was optimized by adjusting the vertical and horizontal controls of the probe carriage to obtain an FID with the longest characteristic decay time T*2. The magnet was then set on resonance and the detector phase adjusted to maximize the amplitude of the FID. This FID was 90° out of phase with the rf pulse.

Typically one hundred data points of Mz(t) were taken in the T1 measurements. The magnetization was sampled for each value of time separation τ between the 180° pulse and 90° pulse which was automatically incremented using the autoincrement module in the pulse programmer. A Biomation waveform recorder was used to collect the FID data. Each FID was processed by digitizing at 256 points. The first few channels were summed in the early part of the FID. Next, several channels were summed in the region of FID baseline. The weighted difference which represented the initial
amplitude of the FID relative to its baseline was then stored in the memory of a Nicolet signal averager. To prevent saturation, the repetition time between successive pulse sequences was set to \(10T_1\). The time interval \(\Delta t\) between the adjacent data points was set approximately equal to \(3T_1/100\) to ensure that the initial part of the magnetization recovery was included in the one hundred data points. In order to extract the spin-lattice relaxation time, the equilibrium magnetization \(M_o\) was also measured. This was done by turning off the 180° pulse in channel 1 and retaining the 90° pulse in channel 2. The average value of one hundred points of \(M_o\) in a single pass was then used in the fit. For analysis, the data were transferred to the Digital Equipment Corporation LSI-11 computer which was interfaced with the Nicolet signal averager.

For a single exponential recovery the magnetization is described by

\[
M_z(t) = M_o [1 - 2 \exp\left(-t/T_1\right)].
\] (3-7)

This equation also enables us to make a rough estimate of \(T_1\), since \(T_1 = \tau/\ln2\) for \(M_z = 0\). A least-squares fit of Equation 3-7 in the form

\[
\ln\left(\frac{M_o - M_z(t)}{2M_o}\right) = -\left(\frac{t}{T_1}\right)
\] (3-8)

was made to the data points.

In \(\text{LaH}_x\) for \(x \geq 2.5\) two proton resonances with different spin-lattice relaxation times were observed to coexist over
some temperature interval. A five-parameter nonlinear least squares fit program was used to fit the non-exponential \( M_z(\tau) \) data. The equation we used is

\[
M_z(\tau) = M_{oL} \left[ 1 - (1 + \alpha) e^{-\tau/T_{1L}} \right] + (M_0 - M_{oL}) \left[ 1 - (1 + \alpha) e^{-\tau/T_{1S}} \right]
\]

(3-9)

where \( M_0 \) is the total magnetization, \( M_{oL} \) is the portion of \( M_0 \) due to spins that relax with time \( T_{1L} \), \( T_{1L} \) and \( T_{1S} \) are the relaxation times of the slow- and fast- relaxing spin components, respectively, and \( \alpha \) is the fraction by which \( M_{oL} \) and \( M_0 - M_{oL} \) are inverted by the 180° pulse at \( \tau = 0 \).

C. Sample Preparation

All the lanthanum hydrides investigated in this work were prepared by B. J. Beaudry and N. Beymer in the Materials Preparation Center of the Ames Laboratory from the highest-purity Ames Laboratory lanthanum metal. The starting pure metal was first analyzed by spark source mass spectrometry. The result of this analysis is summarized in the Appendix which shows that it contained very low levels of paramagnetic rare-earth impurities before it was doped with controlled levels of gadolinium. The doping was accomplished by two steps. First, an arc-melted sample contained one atomic percent solute was prepared, and it was then diluted by remelting with additional La to give the lower solute levels (25 - 300 ppm).
The lanthanum metal or alloy was carefully electropolished and placed in a platinum boat. The hydriding process was carried out in a standard high pressure, high vacuum system which was pumped down to $2 \times 10^{-7}$ torr before heating the metal. Mischmetal trihydride served as a source of high-purity hydrogen. The metal was heated to about $400^\circ$C in vacuum and then exposed to the hydrogen gas for reaction. To ensure complete homogeneity, the sample was heated up to $500^\circ$C, and the existence of the equilibrium partial pressure was then monitored. The rather brittle sample was crushed in a mortar in a helium filled drybox and sealed in a quartz tube. The hydrogen concentration was initially determined from the pressure change in a known volume of gas and from the increase in weight of the sample on hydriding. Final determination of the composition was made by vacuum extraction of the hydrogen from a portion of the sample at high temperature.
Figure 3.4 A 90° pulse and the resulting behavior of the nuclear magnetization; (a) a 90° rf pulse along the x'-axis rotates the magnetization \( \vec{M} \) from the equilibrium position (along z'-axis) to the y'-axis; (b) after \( H_1 \) is turned off, the inhomogeneity of the local field distribution causes the magnetization in the x'y'-plane to dephase; (c) free induction decay (FID) after the 90° pulse is turned off.
Figure 3.5 Determination of $T_1$ by $180^\circ$-\(\tau\)-90° sequence:
(a) the $180^\circ$ pulse inverts the magnetization $\mathbf{M}$ so that $\mathbf{M}(\tau) = -M_0$; (b) after a variable delay time $\tau$, the growing $z$-component of the recovering magnetization is tipped into the XY-plane by a 90° pulse; (c) a schematic of the $180^\circ$-\(\tau\)-90° pulse sequence that constitutes the inversion recovery $T_1$ measurement technique; (d) the initial amplitude of the FID after the $180^\circ$-\(\tau\)-90° pulse sequence, which is proportional to the value of magnetization $\mathbf{M}$ at time $\tau$, is plotted as a function of $\tau$. 
IV. RESULTS AND DISCUSSION

The proton spin-lattice relaxation time $T_1$ was measured over the temperature range 7 K to 670 K on a series of lanthanum hydrides LaH$_x$ with $2.0 \leq x \leq 3.0$, which is in the metal-nonmetal transition region. In addition to pure samples, lanthanum hydrides with controlled levels of gadolinium impurity were also investigated.

The process of proton relaxation in lanthanum hydrides consists of three principal mechanisms: the interaction of protons with conduction electrons, the interaction arising from the fluctuating nuclear dipolar field and the contribution from paramagnetic impurities. The proton has no electric quadrupole moment (since $I=1/2$), so the quadrupole interaction can be excluded. The total spin-lattice relaxation rate $R_1$, which is the reciprocal of $T_1$, can be written as

$$R_1 = R_{1e} + R_{1d} + R_{1p}$$  \hspace{1cm} (4-1)

where $R_{1e}$ is the conduction electron contribution, $R_{1d}$ is the dipolar contribution and $R_{1p}$ is a contribution from paramagnetic impurities. The conduction electron contribution is dependent on the density of states of conduction electrons at the Fermi level, according to the Korringa relation,

$$(T_{1e}T)^{-1/2} \propto N(E_F).$$  \hspace{1cm} (4-2)

In the usual case, the density of states at the Fermi level is
not strongly temperature dependent, and hence Equation 4-2 can be usually written as

\[ T_1 \cdot T = \text{constant,} \quad (4-3) \]

where the constant is called the Korringa product.

The dipolar contribution \( R_{1d} \) is very sensitive to hydrogen diffusion, and therefore can be used to determine the activation energy of the diffusive motion and the temperature dependence of the hydrogen jump frequency. The impurity-induced relaxation rate \( R_{1p} \) was assumed to be very small and temperature independent in many cases reported in the literature. Recently, the temperature dependence of \( R_{1p} \) has been studied systematically for some metal hydrides by Phua et al.\(^{29}\). In particular, the behavior of the \( \text{Gd}^{3+} \) induced relaxation rate in lanthanum hydrides has been clearly understood. Through the dipolar interaction between impurity ion and proton moments, the spin-lattice relaxation rate \( R_1 \) of the hydrogen spin system is expected to depend on the ion spin-lattice relaxation time \( \tau_1 \). This interrelationship was one of the factors that motivated us to study the metal-nonmetal transition in the lanthanum hydrides, LaH\(_x\), \( 2.0 \leq x \leq 3.0 \).

Accordingly, data sets of proton spin-lattice relaxation times were obtained for a series of lanthanum hydrides, both with and without controlled levels of gadolinium impurity. Now it is appropriate to begin the discussion with the data
for the proton resonance in the pure samples.

A. Pure Lanthanum Hydrides LaH$_x$, 2.0 $\leq$ $x$ $\leq$ 3.0

Measurements of the proton spin-lattice relaxation time on a series of pure lanthanum hydrides LaH$_x$ with $x$ = 2.0, 2.35, 2.50, 2.55, 2.60, 2.70, 2.75, 2.80, 2.90 and 3.0 are presented and discussed in this section. These lanthanum hydrides were prepared from the purest lanthanum available in the Ames Laboratory, identification number La-4783. The major paramagnetic impurities total less than 4.5 ppm. The spark-source mass spectrometric analysis of the lanthanum metal is given in the Appendix. The proton T$_1$'s of these samples are plotted on a logarithmic scale as a function of the reciprocal of the absolute temperature in Figures 4.1-4.10. Several qualitative features of these data are worth noting. First, a minimum in this kind of plot clearly shows that proton diffusion provides the dominant relaxation mechanism in this temperature region. Second, the temperature of the minimum spin-lattice relaxation time, T$_{1,min}$, decreases as the hydrogen concentration increases. Third, T$_{1,min}$ decreases with increasing hydrogen concentration. And fourth, two proton spin-lattice relaxation times are observed in LaH$_x$ for $x$ $\geq$ 2.50 over some temperature range in the vicinity of 150 K to 270 K depending on the hydrogen concentration.
Figure 4.1 The logarithm of the proton spin-lattice relaxation time $T_1$ at 40 MHz versus reciprocal temperature ($1000/T$) in LaH$_{2.00}$. 
Figure 4.2 The logarithm of the proton spin-lattice relaxation time $T_1$ at 40 MHz versus reciprocal temperature ($1000/T$) in LaH$_{2.35}$. The broken line is the least-squares fit using a BPP function and a temperature independent Korringa constant. The fitting parameters are given in the text.
Figure 4.3 The logarithm of the proton spin-lattice relaxation time $T_1$ at 40 MHz versus reciprocal temperature (1000/T) in $\text{LaH}_2.50$. The open triangle represents $T_1$ of the second phase.
Figure 4.4 The logarithm of the proton spin-lattice relaxation time $T_1$ at 40 MHz versus reciprocal temperature (1000/T) in LaH$_{2.55}$. The open triangle represents $T_1$ of the second phase.
Figure 4.5 The logarithm of the proton spin-lattice relaxation time $T_1$ at 40 MHz versus reciprocal temperature (1000/T) in LaH$_2$. The open triangle represents $T_1$ of the second phase.
Figure 4.6 The logarithm of the proton spin-lattice relaxation time $T_1$ at 40 MHz versus reciprocal temperature (1000/T) in La$H_{2.70}$. The open triangle represents $T_1$ of the second phase.
Figure 4.7 The logarithm of the proton spin-lattice relaxation time $T_1$ at 40 MHz versus reciprocal temperature (1000/T) in LaH$_{2.75}$. The open triangle represents $T_1$ of the second phase.
Figure 4.8 The logarithm of the proton spin-lattice relaxation time $T_1$ at 40 MHz versus reciprocal temperature ($1000/T$) in LaH$_{2.80}$. The open triangle represents $T_1$ of the second phase.
Figure 4.9 The logarithm of the proton spin-lattice relaxation time $T_1$ at 40 MHz versus reciprocal temperature (1000/T) in $\text{LaH}_2.90$. The open triangle represents $T_1$ of the second phase.
Figure 4.10 The logarithm of the proton spin lattice relaxation time $T_1$ at 40 MHz versus reciprocal temperature ($1000/T$) in LaH$_{3.00}$. The open triangle represents $T_1$ of the second phase.
In a truly pure sample, $R_{1p}$ can be neglected so that 

$$R_i = R_{1e} + R_{1d}. \quad (4-4)$$

At sufficiently low temperature where the hydrogen diffusion is insignificant, $R_{1d} \ll R_{1e}$, so that the measured $R_i = R_{1e}$. By using the Korringa relation, $T_{1e}T = \text{constant}$, the values of $T_{1e}$ at higher temperatures can be calculated from the low temperature results. Consequently, the diffusion-controlled rate $R_{1d}$ can be obtained by subtracting $R_{1e}$ from the measured $R_i$. From the temperature dependence of $R_{1d}$ information regarding hydrogen diffusion can be extracted.

1. **Electronic density of states**

   In the case of LaH$_{2.00}$ (Figure 4.1), the curve of $\log(T_1)$ versus 1000/T shows that the conduction-electron contribution $R_{1e}$ is the dominant relaxation mechanism at temperatures below ~300 K. This region is called the rigid-lattice regime. In this low temperature region the values of $T_1$ increase with decreasing temperature, similar to Phua's data$^6$ but in contrast to Schreiber and Cotts' data$^2$. This fact indicates that the Ames Lab samples do not contain high levels of paramagnetic impurities, since it is apparent that in Schreiber and Cotts' samples relaxation by paramagnetic impurities dominates at low temperatures. As the temperature increases, the thermally activated diffusive motion of the hydrogen becomes more rapid, thus, the proton spin-lattice
relaxation time $T_1$ is sharply decreased and is expected to reach a minimum as has been outlined in Chapter II. Phua's data\textsuperscript{60} show an obvious although very weak subsidiary minimum or "slope-change" on the low temperature side of the principal diffusion minimum, whereas this is not seen in our data. This observation is indeed consistent with his conclusion\textsuperscript{29} that in a truly impurity-free metal hydride, only a single minimum in the temperature dependence of the proton $T_1$ would be obtained without any indication of a secondary minimum or change in slope on the low temperature side of the minimum. As determined by mass-spectrographic analysis the lanthanum metal used in this work contains a total rare-earth impurity content of less than 4.5 parts per million (ppm) compared to 15.6 ppm in Phua's samples.

Figure 4.11 shows a plot of the total relaxation rate $R_1$ for LaH$_{2.0}$ in the rigid-lattice regime versus temperature. In this temperature region, $R_1 = R_{1e} + R_{1p}$, and $R_{1p}$ is nearly independent of temperature (as will be seen in section B). The slope of the straight line gives the Korringa product $T_{1e}T = 411$ s K, and the intercept on the $R_1$ axis gives the impurity induced rate $R_{1p} = 0.215$ s$^{-1}$. This result may be compared with $T_{1e}T = 305$ s K in Phua's thesis. The Korringa product is related to the electronic density of states at the Fermi level by the relation $(T_{1e}T)^{-1/2} \propto N(E_F)$. Although the constant of proportionality is not readily established for hydrogen in
Figure 4.11 Temperature dependence of the measured proton spin-lattice relaxation rate $R_1$ in LaH$_{2.00}$ at low temperatures measured at 40 MHz. The solid line is the least-squares fit to the straight-line portion of the data. The fitting parameters are showing on the figure.

$$R_1 = 0.00243 T + 0.215 \text{ s}^{-1}$$

$$T_{1e} T = 411 \text{ sK}$$
metals, \((T_1 \cdot T)^{-1/2}\) provides a quantitative indication of the relative behavior of \(N(E_F)\) in metal hydrides. The values of the Korringa product \(T_1 \cdot T\) obtained from the present measurements are listed in Table 4-1. The values of \(T_1 \cdot T\) obtained here are compatible with recent measurements\(^6\) in which the technique of partial deuteration was utilized to suppress the paramagnetic impurity contribution to the spin-lattice relaxation rate, yielding \(T_1 \cdot T = 405\) s K for \(\text{La(\text{HD})}_{2.25}\) and \(T_1 \cdot T = 415\) s K for \(\text{LaD}_{2.65}\). For the samples with \(x \geq 2.7\) the Korringa products could not be determined with accuracy for several reasons. First, even the very low levels of residual rare-earth impurities have relatively strong effects for weakly metallic and insulating samples. Second, the rigid-lattice regime might still not be reached at the lowest temperature measured, or the Korringa relation might not be obeyed for the trihydride phase. Also, the relatively long \(T_1\) makes the measurements more difficult. However, the values of the product \(T_1 \cdot T\) at 147 K are listed for comparison.

As seen in Figure 4.12, the behavior of \((T_1 \cdot T)^{-1/2}\) versus \(x\) implies that \(N(E_F)\) decreases with increasing hydrogen concentration consistent with the anticipated insulating (or semiconducting) character of \(\text{LaH}_x\) as \(x\) approaches 3. Also shown is a curve based on the free-electron density-of-states that goes as \((3 - x)^{1/3}\). The curve is fit at \(x = 2.6\). It
Figure 4.12 Plot of \((T_1 T)^{-1/2}\) as a function of hydrogen concentration for \(\text{LaH}_x\). The open crosses are \((T_1 T)^{-1/2}\) values at 147 K. The broken line shows a curve based on the free-electron density-of-states going as \((3 - x)^{1/3}\).
follows the data quite well and shows that the density of states is following free-electron behavior at least up to $x = 2.8$. For LaH$_{2.0}$, the $R_1$ graph shown in Figure 4.11 indicates a substantial impurity rate contribution, so this point in Figure 4.12 cannot be taken too seriously.

We may compare Figure 4.12 with the Knight shift of the lanthanum resonance which also gives information on the electronic structure. In the work of Schreiber and Cotts$^2$ the La Knight shift at 400 °C decreased with hydrogen concentration and was expected to go to zero at LaH$_3$. However, a more recent measurement of the La shift by Barnes et al.$^{28}$ indicated that in LaH(D)$_3$ the shift remains about 0.10% for temperatures above 210 K rather than going to zero for $x$ approaching 3.0. Figure 4.13 shows the original measurements of Schreiber and Cotts together with some of the results by Barnes et al. at high $x$ values. The solid curve is based on the free-electron density-of-states, fit at $x = 2.4$. Again, the first point that departs significantly from free-electron behavior is at $x = 2.9$. Another parameter that reflects the behavior of the electronic density-of-states is the electronic specific-heat constant $\gamma$. Low-temperature specific-heat measurements of LaH$_x$ ($1.9 < x < 3.0$) have been undertaken by Gschneidner and co-workers$^{62}$. The composition dependence of the electronic specific-heat constant $\gamma$ is shown in Figure 4.14. Surprisingly, the decrease of $\gamma$ is nearly a
Figure 4.13 Concentration dependence of lanthanum Knight shift in $\text{LaH}_x$. Solid curve is the free-electron approximation.
Figure 4.14 Concentration dependence of the electronic specific-heat constant $\gamma$ of LaH$_x$, Ref. 62.
Table 4-1. The Korringa products and relative density-of-states for lanthanum hydrides LaHₓ

<table>
<thead>
<tr>
<th>x=[H]/[La]ᵃ</th>
<th>T₁ₑT (s-K)ᵇ</th>
<th>(T₁ₑT)⁻¹/² (s-K)⁻¹/²</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>411</td>
<td>.049</td>
</tr>
<tr>
<td>2.35</td>
<td>454</td>
<td>.047</td>
</tr>
<tr>
<td>2.50</td>
<td>568</td>
<td>.042</td>
</tr>
<tr>
<td>2.55</td>
<td>537</td>
<td>.043</td>
</tr>
<tr>
<td>2.60</td>
<td>595</td>
<td>.041</td>
</tr>
<tr>
<td>2.70</td>
<td>736*</td>
<td>.037</td>
</tr>
<tr>
<td>2.80</td>
<td>900*</td>
<td>.033</td>
</tr>
<tr>
<td>2.90</td>
<td>1083*</td>
<td>.030</td>
</tr>
</tbody>
</table>

ᵃEstimated uncertainty in [H]/[La] is about ±0.02.
ᵇEstimated uncertainty in T₁ₑT is about ±5 s-K.
*T₁ₑT product at 147 K.
linear function of $3-x$ rather than of $(3 - x)^{1/3}$. Almost no electronic contribution to the heat capacity is observed for LaHo.

2. $T_{d}$ minimum

In the rigid-lattice regime, the protons are fixed in the interstitial sites of the fcc lanthanum metal lattice. At higher temperatures the protons jump from one interstitial site to another with a frequency $\nu_0 = 1/\tau_0$. The dipolar interaction between protons and between protons and lanthanum moments is modulated by this motion providing an effective spin-lattice relaxation mechanism. The proton spin-lattice relaxation rate for the situation in which both like and unlike spins (the La nuclei) interact, is given by

$$R_{1d} = \frac{3}{2} \gamma_1^2 \hbar^2 \mathbb{I}(I+1) \left[ J^{(1)}(\omega_l) + J^{(2)}(2\omega_l) \right]$$
$$+ \gamma_1^2 \gamma_S^2 \hbar^2 S(S+1) \left[ \frac{1}{12} J^{(0)}(\omega_l - \omega_S) \right.$$
$$\left. + \frac{3}{2} J^{(1)}(\omega_l) + \frac{3}{4} J^{(2)}(\omega_l + \omega_S) \right]$$

(4-6)

where $J^{(q)}(\omega)$ are the spectral density functions. The spin values are denoted by $I$ and $S$ and the gyromagnetic ratios are given by $\gamma_1$ and $\gamma_S$ for the proton and the lanthanum nucleus, respectively. Since the fcc lattice has very high symmetry, isotropy is assumed. If one adopts the BPP model (Equation 2-14), the spectral density function

$$J^{(1)}(\omega) = \frac{2}{15}(2\tau_c/1+\omega^2\tau_c^2) r_1^{-6}$$

(4-7)

and

$$J^{(2)}(\omega) : J^{(1)}(\omega) : J^{(0)}(\omega) = 4 : 1 : 6$$

(4-8)
for a powder sample, where the sum Σ extends to occupied spin sites.

Since the lanthanum nuclei are fixed in place, the proton-metal dipolar field correlation time τc is equivalent to τb, the mean dwell time of a proton at a given site. On the other hand, the proton-proton dipolar field correlation time τc = τb/2 because either proton is moving about. Equation 4-6 can be expressed in terms of the second moment which is a measure of the mean square width of a broadened proton resonance line. The second moments arising from the dipolar interaction between ¹H - ¹H and ¹H - ¹³⁹La for the powder sample are

\[ M_{I1} = (3/5)\xi_I^2 \mu_1^2 I(I+1) \sum r_i^{-6} \]  
\[ M_{I5} = (4/15)\xi_5^2 \mu_5^2 S(S+1) \sum r_j^{-6}, \]

respectively. The sum \( \sum r_i^{-6} \) is over all hydrogen sites i and \( \sum r_j^{-6} \) is over all metal sites j from a typical hydrogen site at the origin. Combining Equation 4-6 to 4-10 we have

\[ R_{i,a} = (4/3)(\xi_1^2 M_{I1}/\omega_1)[y/(4+y^2) + y/(1+y^2) + (3/8)(M_{I5}/M_{I1})] \]
\[ [y/(1+f^2y^2) + 3y/(1+y^2) + 6y/(1+g^2y^2)]. \]

Here, \( \xi_1 \) is the proton gyromagnetic ratio, \( \omega_1 \) and \( \omega_5 \) are the Larmor frequencies for the proton and lanthanum nucleus, respectively, and \( y = \omega_1 \tau_0 \). The factors \( f = 1 - \omega_5/\omega_1 \) and \( g = 1 + \omega_5/\omega_1 \) in which the ratio of the Larmor frequency of the La nucleus to that of the proton \( \omega_5/\omega_1 = 0.14 \). The \( R_{i,a} \) maximum (or \( T_{i,a} \) minimum) occurs at the temperature where \( {} \) in Equation 4-11 reaches its maximum value.
Now we develop the expressions for the proton second moment to calculate the values of the T₁₄ minimum in LaHₓ from Equation 4-11. Assume that the interstitial sites are randomly occupied by protons at high temperatures. This is similar to the calculations made by Schreiber and Cotts to estimate the fractional occupation of the O-sites.

Let α and β be the probabilities of occupancy of octahedral and tetrahedral sites, respectively. Because there are two tetrahedral sites for each octahedral site, the fractions of protons in each site are

\[ f_{\text{oct}} = \frac{\alpha}{2\beta + \alpha} \quad \text{and} \quad f_{\text{tet}} = \frac{2\beta}{2\beta + \alpha}. \] (4-12)

Therefore \( x = 2\beta + \alpha \) in LaHₓ. Then the total second moment is just the weighted sum of the second moments for the two types of sites. Thus Equations 4-9 and 4-10 can be written as

\[
M_{\text{t}} = \frac{3}{5} \gamma \sum_{i}^{\text{oct}} \frac{1}{2} (\alpha \sum_{i}^{\text{tet}} r_{i}^{-6} + \beta \sum_{i}^{\text{tet}} r_{i}^{-6}) \]

\[
M_{\text{t}} = \frac{4}{15} \gamma \sum_{k}^{\text{host}} (\alpha \sum_{k}^{\text{tet}} r_{k}^{-6} + \beta \sum_{k}^{\text{tet}} r_{k}^{-6}) \]

where the sums, \( \sum_{i}^{\text{oct}} \), \( \sum_{j}^{\text{tet}} \), and \( \sum_{k}^{\text{host}} \) are over octahedral, tetrahedral and host metal sites, respectively. By using the known values of \( \gamma \) and \( \gamma' \), the spins of H and La, and the lattice sums evaluated in terms of the lattice constant \( a_{0} \), Equations 4-13 and 4-14 become

\[
M_{\text{t}} = (3.58 \times 10^{-4} a_{0}^{-6}) / (2\beta + \alpha) \left[ 115.6 a^{2} + 2640 \alpha \beta + 1075 \beta^{2} \right] \]

and

\[
M_{\text{s}} = (0.667 \times 10^{-6} a_{0}^{-6}) / (2\beta + \alpha) \left[ 422 \alpha + 1321 \beta \right],
\]

where \( M_{\text{t}} \) and \( M_{\text{s}} \) are in units of G² if \( a_{0} \) is in cm.
In \( \text{LaH}_x \), \( x \geq 2 \), we ignore the approximately 5% premature occupancy of O-sites\(^2\) and assume that all tetrahedral sites are occupied and the octahedral sites are occupied randomly to become full at \( x = 3 \). Then \( \beta = 1 \) and \( \alpha = x - 2 \) in this concentration range. From the calculations, it is found that the contribution from the lanthanum nuclei \( M_{ls} \) is small compared to that from the protons \( M_{li} \) in the trihydride phase. For example, the ratio \( M_{ls}/M_{li} = 11\% \) in \( \text{LaH}_2.50 \) and only 8.5% in \( \text{LaH}_3.00 \). Consequently, the dipolar relaxation of the protons results primarily from the coupling between the protons. The proton spin-lattice relaxation rate due to hydrogen diffusion in Equation 4-11 can therefore be taken approximately as

\[
R_{1d} = \frac{2}{3} \left( \frac{\gamma T^2 M_{li}}{\omega} \right) \left[ \omega T c / (1 + \omega T ^2 T c ^2 ) \right] + 4 \omega T T c / (1 + 4 \omega T ^2 T c ^2 )
\]

where \( T c = T D / 2 \), with \( T D = T 0 \exp(E_s / k_B T) \). For \( \omega T T c = 0.616 \), the function in \(
\) is maximized at the value 1.425 so that it causes a minimum in \( T_{1d} \). Figure 4.16 shows the calculated and observed values of \( T_{1d, min} \) as a function of \( x = [H]/[\text{La}] \). In the calculation the dependence of lattice parameter \( a_0 \) on the hydrogen concentration has been taken into account according to the results of Klavins et al.\(^1\). For all compositions except \( x = 2.9 \) and 3.0 the calculated \( T_{1d, min} \) are in satisfactorily good agreement with the observed values. The small discrepancy results from the contributions from
lanthanum nuclear moments and residual paramagnetic impurities.

For $x = 2.9$ and $3.0$ the observed values are unusually higher than expected. However, the calculations are based on the high-temperature, disordered O-site occupancy of protons and since in $x = 2.9$ and $3.0$ the minima of the high-temperature single component $T_1$ values are not reached before the two-component regions are reached, there is no reason to suppose that the $T_{1,\text{min}}$ for these compositions are anomalous. In fact, the high-temperature single-component $T_1$ values for $x = 2.9$ and $3.0$ are progressing toward minima which are at temperatures and $T_{1,\text{min}}$ values that are what were anticipated (see Figure 4.15, for example). These values form a continuation of the trend for all the other $T_{1,\text{min}}$ data points (Figures 4.16 and 4.17). In order to check this, the proton $T_1$ in LaH$_2.90$ was measured at 65 MHz. According to Equation 4-17 the temperature of $T_{1,\text{min}}$ shifts to higher temperature and the value of $T_{1,\text{min}}$ is proportional to the proton resonance frequency $\omega_1$. If the true $T_{1,\text{min}}$ at 40 MHz is 26.6 ms as calculated, the value of $T_{1,\text{min}}$ at 65 MHz is 43 ms. The observed value of 39 ms at $T = 278$ K is in good agreement with this. Therefore, there is no anomalous behavior of the high-temperature phase $T_{1,\text{min}}$ for $x = 2.9$ and $3.0$ except that its observation at 40 MHz is obscured by the onset of two-component behavior.
Figure 4.15 The logarithm of the proton spin-lattice relaxation time $T_1$ at 40 MHz versus reciprocal temperature (1000/T) in LaH$_{2.90}$. The broken line is the least-squares fit to the high-temperature data points using a BPP function with the value of $T_1,m,n$ fixed at the calculated value.
Figure 4.16 Comparison of the experimental proton $T_{1d}$ minimum at 40 MHz for LaH$_x$ with the prediction of Eq. 4-17.
Figure 4.17 Concentration dependence of the temperature of T$_{1\text{d, min}}$ measured at 40 MHz for LaH$_x$. 
3. Diffusion parameters

Samples used in this work were prepared from starting lanthanum metal of high purity, so the impurity-induced relaxation rate is negligible. The total proton spin-lattice relaxation rate is the sum of the diffusion-controlled rate and the conduction-electron contribution as seen in Equation 4-4. Analysis of the experimental relaxation rates of lanthanum trihydrides is not an easy task. The complexity results from the coexistence of two proton resonances having different spin-lattice relaxation rates over some temperature range and from the occurrence of electronic phase transition.

In LaH\textsubscript{2.33} a single T\textsubscript{1} was observed for all temperatures investigated. The BPP function for R\textsubscript{1d} (Equation 4-17) plus a Korringa term were used to fit the T\textsubscript{1} data. The result of this fit is shown in Figure 4.2. The best fit parameters are the following: \( E_a = 0.35 \text{ eV/atom} \), \( \tau_{00} = 6.2 \times 10^{-13} \text{ s} \), \( T_{1d,\text{min}} = 38.4 \text{ ms} \) and \( T_{1cT} = 454 \text{ s-K} \). The results show that the LaH\textsubscript{2.33} sample has very high purity and that the hydrogen diffusive motion is characterized by a single correlation time.

For hydrogen concentrations \( x \geq 2.50 \) the coexistence of two spin-lattice relaxation times implies the presence of two phases. Hydrogen in the two phases has different diffusion rates. In those samples with \( 2.5 \leq x \leq 2.8 \) the high-
temperature single-phase $T_1$ passes through a minimum before the two-phase region is reached and thus the diffusion parameters of the high-temperature phase can be determined by fitting the $T_1$ data. Since lanthanum hydrides LaH$_x$ become less metallic as $x$ approaches 3, the conduction-electron contribution to the spin-lattice relaxation rate may not obey the Korringa relation any more. Even if the Korringa relation is observed at low temperatures, it may not be appropriate to extend this Korringa constant to the high-temperature phase before the natures of the different phases are understood. Therefore, not too much reliance should be placed on Korringa constants obtained from the fit; instead attention is directed to the values of $E_a$ and $w_0$.

The results are tabulated in Table 4-2. The activation energies and jump frequencies obtained here are consistent with the results of Phua$^{60}$ for comparable compositions in the dihydride phase. Table 4-2 shows unambiguously that the activation energy decreases with increasing hydrogen concentration. Also the jump frequencies of the proton motion at 300 K indicate that an increase in hydrogen concentration enhances the proton motion. This observation had already been reported by Schreiber and Cotts$^{27}$ in their pioneer work on lanthanum hydrides. To understand the dependence of $E_a$ on hydrogen concentration an explicit knowledge of the hydrogen-metal interaction would have to be known because $E_a$ is
Table 4-2. Diffusion parameters: activation energy $E_a$, attempt frequency $\nu_{D0}$, jump frequency at $300K\nu_{D}$ (300K), for hydrogen in LaH$_x$ obtained using the BPP function

<table>
<thead>
<tr>
<th>$X = [H]/[La]$</th>
<th>$E_a$ (eV/atom)</th>
<th>$\nu_{D0}$ $s^{-1}$</th>
<th>$\nu_D$ (300K) $s^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.35</td>
<td>0.35</td>
<td>$1.6 \times 10^{12}$</td>
<td>$2.1 \times 10^6$</td>
</tr>
<tr>
<td>2.50</td>
<td>0.28</td>
<td>$1.1 \times 10^{12}$</td>
<td>$2.2 \times 10^7$</td>
</tr>
<tr>
<td>2.55</td>
<td>0.25</td>
<td>$6.7 \times 10^{11}$</td>
<td>$4.2 \times 10^7$</td>
</tr>
<tr>
<td>2.60</td>
<td>0.21</td>
<td>$4.2 \times 10^{11}$</td>
<td>$1.2 \times 10^8$</td>
</tr>
<tr>
<td>2.70</td>
<td>0.18</td>
<td>$3.4 \times 10^{11}$</td>
<td>$3.2 \times 10^8$</td>
</tr>
<tr>
<td>2.75</td>
<td>0.19</td>
<td>$5.9 \times 10^{11}$</td>
<td>$3.8 \times 10^8$</td>
</tr>
<tr>
<td>2.80</td>
<td>0.18</td>
<td>$4.5 \times 10^{11}$</td>
<td>$4.3 \times 10^8$</td>
</tr>
<tr>
<td>2.90</td>
<td>0.15</td>
<td>$2.5 \times 10^{11}$</td>
<td>$7.6 \times 10^8$</td>
</tr>
</tbody>
</table>
associated with the potential barrier to the hydrogen motion that arises from its interaction with the surrounding atoms. Schreiber suggested a highly simplified point charge model using spherical charge distributions to calculate Coulomb energies at each interstitial site. In his model it is assumed that the hydrogen is essentially ionized and that its electron goes into the conduction band which is made of the 5d6s bands of lanthanum, and that $E_a$ is the proton's change of energy from one site to another. Qualitatively, the addition of one occupied octahedral site will lower the energy barrier of each of its eight nearest-neighbor protons because of the Coulomb repulsion, and this makes the protons in the adjacent tetrahedral sites likely to jump into one of the next unoccupied octahedral sites. This model is fairly successful in the prediction of the concentration dependence of $E_a$ and the $E_a$ values for concentrations near 2, but the $E_a$ values obtained from Ti data in his report are relatively unreliable due to the high impurity concentrations in the samples.

The increase of hydrogen diffusion with increasing hydrogen concentration in lanthanum hydride is in contrast to the behavior of some of the transition metal hydrides such as ScH$_x$, ZrH$_x$ and TiH$_x$ in which hydrogen diffusion decreases with increasing hydrogen concentration. In the latter case the hydrogen diffusion is slowed down as more hydrogen is introduced due to the site-blocking effect.
However, as pointed out by Phua\(^6\) the accessibility of the octahedral sites changes the situation. For some transition metal dihydrides in which the spacing between the T-site and O-site is shorter than 2.10 Å, the trihydride phase has never been obtained, and therefore the O-sites are not energetically accessible for hydrogen occupancy. Since for \(x \leq 2.0\) only T-sites are occupied, the hydrogen diffusion becomes very slow as \(x = 2\) is approached because of the blocking factor \((2-x)\). On the other hand, for those metal hydrides in which the spacing between the T-site and O-site is larger than 2.10 Å, the trihydride phase can be reached, and evidently O-sites are available for hydrogen occupancy. As more hydrogen is introduced in the O-sites, the energy barrier to hydrogen motion between O-sites and T-sites is lowered by Coulomb repulsion, and the diffusive motion occurs more readily.

4. Coexistence of two proton resonances

In common with the trihydrides of the other light rare-earth elements (i.e., Ce, Pr and Nd), lanthanum trihydrides exhibit two co-existing proton resonances in certain temperature regions. Such behavior was first observed by Schreiber and Cotts\(^2\). The temperature dependence of the wide-line proton resonance was investigated in most of the samples. Two resonances are clearly distinguished within some temperature
range. Figure 4.18 shows an example of this behavior for LaH$_{2.60}$, at T = 182, 172 and 167 K. With decreasing temperature, the narrow proton resonance observed at 300 K broadens gradually. Beginning at about 200 K, a broad resonance appears superimposed on the narrow line, and both resonances remain observable for a further decrease of about 40 K after which the two lines cease to be distinguishable. It is also evident from the figure that the two resonances are unshifted with respect to each other. This fact is also very evident in the pulse measurements of T$_1$ in that the entire FID can be brought into resonance at the same time.

In T$_1$ measurements it has been found that the two resonances have different spin-lattice relaxation times, corresponding to the two components in the FID (Figure 4.19). The slow-decaying component of the FID has the shorter T$_1$. This is consistent with the result of an experiment by Creel$^{69}$ which demonstrates that the narrow line has the shorter T$_1$ (Figure 4.20). On the basis of the T$_1$ measurements, a diagram was constructed, showing the regions of temperature and composition within which two signals are observed (Figure 4.21). Also shown are the temperatures at which the tetragonal distortion occurs in the lanthanum lattice as detected by x-ray diffraction$^{19}$.

For all samples, no temperature-dependent transition in T$_1$ is ever found. The high-temperature T$_1$ and the short-T$_1$
Figure 4.18 First-derivative continuous-wave NMR spectra of $^1$H in LaH$_{2.60}$ for three temperatures, 182, 172 and 167 K. Data are recorded at a Larmor frequency of 16.1 MHz. Two lines are observable at each temperature.
Figure 4.19 The free-induction decay (FID) of $^1$H magnetization in LaH$_{2.99}$ at $T = 196.1$ K observed at 40 MHz, showing two components with different decay rates.
Figure 4.20 Fourier transform inversion recovery sequence demonstrating that narrow resonance has shorter $T_1$ than wide resonance. Time intervals are between 180° inversion pulse and 90° sampling pulse.
Figure 4.21 "Phase diagram" based on NMR T$_i$ measurements. '▲' shows the temperature at which two T$_i$'s are first detected with decreasing temperatures; '▼' shows the temperature at which two T$_i$'s are no longer detectable; '●' shows the temperature at which tetragonal distortion of the lanthanum lattice is first detected by X-ray diffraction.
component $T_i$'s join continuously. This kind of feature is not unique at 40 MHz, but is also found at 65 MHz, 24 MHz and 12 MHz in measurements on LaH$_2$. With decreasing temperature, the fast-decaying component of the FID having the longer $T_i$ appears superimposed on the high-temperature component. For $2.5 \leq x \leq 2.8$, the intensity of this long-$T_i$ component increases first and then decreases with further decreasing temperature. The maximum intensity ranges from $10\%$ to $80\%$ of the total magnetization, depending on the hydrogen composition. In contrast, the intensity of the long-$T_i$ component increases monotonically for $x = 2.9$ and 3.0 as the temperature decreases. Below about 170 K we again have a single $T_i$ for all compositions. The component which persists below this temperature is the short-$T_i$ component, except for $x = 2.9$ and 3.0 in which it appears to be the long-$T_i$ component that persists.

The proton spin-lattice relaxation times in the two-component regions behave in quite different ways for $x < 2.6$ and $x > 2.6$ when we compare the co-existing $T_i$'s with that extrapolated from the high-temperature $T_i$ value (see Figures 4.3 to 4.10). At $x = 2.6$, there appears to be nearly a one-component system. For $x > 2.6$, the two $T_i$'s are both greater than the value extrapolated from high temperatures and yield activation energies which are greater than those of the high-temperature curves. For $x = 2.50$ and 2.55 the short $T_i$ value
lies below the extrapolated curve.

Now the basic question is, "What is the origin of the two proton resonances?". Evidently, it is not sample inhomogeneity because it is not observed in samples with \( x < 2.5 \). Next, it might be the presence of crystalline and amorphous phases. In order to examine this possibility, a measurement of \( T_1 \) was made on a predominantly amorphous \( \text{LaH}_2 \cdot 99 \) sample (kindly provided by Prof. E. Kaldis of the ETH, Zurich, Switzerland) over the temperature range 300-150 K. The results again show two \( T_1 \)'s and appear very similar to the measurement on the Ames Laboratory sample (Figure 4.22). Since we do not really know how crystalline the Ames Laboratory samples are, this possibility cannot be ruled out. Alternatively, the two resonances might arise from coexistence of the metal and semiconductor phases if there is a temperature-dependent transition. The difference in relaxation rates in the two phases is not found to have a constant \( T_1 \cdot T \) term. However, in addition to the small difference in conduction-electron contribution, a difference in hydrogen diffusion rates in the two phases would most likely account for the difference in \( T_1 \) values. Another possibility is that the two resonances arise from hydrogen in the tetrahedral and octahedral interstitial sites if these have different diffusion rates and if the possibility of hopping from one type of site to the other is low. If so,
Figure 4.22 Comparison of log $T_1$-vs-$1000/T$ plots for proton at 40 MHz in lanthanum trihydride samples prepared at Ames Laboratory and at ETH Zurich.
this should also be observed for samples with $[\text{H}]/[\text{La}] < 2.5$. However, as seen in Figure 4.2 only a single $T_1$ is observed for $\text{LaH}_2.3$, showing that all the hydrogen moves equivalently. Also, since the tetrahedral and octahedral sublattices are interpenetrating, it seems unlikely that hydrogen in the two types of site moves independently.

A possible solution to this question lies on the ordering of the O-site hydrogen. Neutron-diffraction studies$^{21}$ of $\text{LaD}_3$ detected superlattice reflections whose intensity was found to increase at temperature below about 250 K. It was suggested that this indicated an ordering of the D atoms on off-center positions within the O-site. The temperature of the onset of the two-resonance region in $\text{LaH}_{3.0}$ is found to be in good agreement with the transformation temperature of the O-site ordering. Moreover, the intensity of the long-$T_1$ component as a function of temperature correlates closely with the extent of the superlattice ordering. The ordered structures may be similar to those in $\text{PdH}_x$ which has an fcc metal lattice with hydrogen occupying octahedral rather than tetrahedral sites. The filling of O-sites in $\text{LaH}_{2+x}$ may correspond to the filling of those sites in $\text{PdH}_x$. Blaschko and co-workers$^{70}$ consider an ordering of O-site D atoms on (420) planes in $\text{PdD}_x$, identical to the ordered state in $\text{Ni}_n\text{Mo}$. There may be a sequence of orderings of hydrogen on the (420) planes as the composition passes through the values of 2.50, 2.67, 2.75 and 2.80 in
Recently, a systematic x-ray diffraction study of the cubic-to-tetragonal structural transformation in the CeH₂-CeH₃ system¹ indicated the presence of two fields of tetragonal distortion, each having a limited concentration range centered around x = 2.35 and 2.75, respectively. Miscibility gaps between the tetragonal and cubic phase exist on both sides of the tetragonal distortion fields. This sort of phase diagram (see Figure 4.23) may explain why nearly single-phase behavior occurs near x = 2.6 as observed in our NMR work.

At this point, the origin of the two NMR signals is difficult to identify. The facts discussed above suggest that it may be associated with the ordering effects of the O-site hydrogen. The two NMR signals may reflect the occurrence of microdomains of two different orderings of hydrogen in these composition and temperature ranges.

B. The La₁₋ₓGdₓHₓ System

Recently, it has been shown that paramagnetic ions, in concentrations so low as to have been regarded as insignificant, have marked effects on the temperature dependence of the proton spin-lattice relaxation time²⁹, ⁷². Among the Kramers ions cerium, neodymium, gadolinium, dysprosium and erbium the S-state ion Gd³⁺ is the most effective in relaxing proton spins. This behavior reflects
Figure 4.23 The T-x phase diagram of CeHx, Ref. 71. (The ratios [H]/[Ce] must be reduced by 0.1 according to the authors' note.)
the fact that the Gd$^{3+}$ ion interacts only weakly with the crystalline electric field (CEF) so that it is itself a relatively slowly relaxing ion. The Gd$^{3+}$-induced proton relaxation in lanthanum hydrides has been shown to be entirely due to the dipolar interaction between impurity ion and proton moments. Protons close to the impurity ions are relaxed directly. Protons far from the impurity ions are relaxed by spin diffusion (mutual spin flips) at low temperatures. With increasing temperature, hydrogen diffusion becomes more rapid than spin diffusion and takes over as the mechanism for transporting distant proton magnetization to the paramagnetic ion. With further increasing temperature, hydrogen diffusion becomes very fast. At this temperature the duration of a single encounter with the impurity ion is too short for efficient relaxation to occur, and the relaxation rate passes through a broad maximum and then decreases slowly with further increasing temperature.

With the understanding of the behavior of the Gd$^{3+}$-induced proton relaxation rate in hand, it is possible to utilize this effect in studying the metal-nonmetal transition in the lanthanum hydride system. In this work the occurrence of the metal-nonmetal transition in lanthanum hydrides has been probed through measurements of the Gd$^{3+}$-induced proton spin-lattice relaxation time.
1. Experimental results

In order to investigate the correlations between the Gd$^{3+}$ ion spin dynamics in lanthanum hydrides and known electrical conductivity changes as a function of hydrogen concentration and temperature, a series of LaH$_x$ with $x = 2.0, 2.35, 2.50, 2.60, 2.70, 2.80, 2.90$ and $3.00$ containing controlled Gd concentrations ranging from 25 ppm to 300 ppm were prepared. The proton spin-lattice relaxation time has been measured as a function of temperature at 40 MHz.

We assume that the various parameters characterizing the motion of the hydrogen and the electronic structure of the hydride are not affected by the presence of the low levels of Gd impurity ions. The relaxation rate due to the Gd$^{3+}$ ions can be obtained by subtracting the rate for the pure sample from that for the Gd-doped sample,

$$R_{1p} = (R_1)_{doped} - (R_1)_{pure}. \quad (4-19)$$

As discussed in section B.3 of Chapter II, the paramagnetic relaxation rate in the case of dilute impurities is proportional to the concentration of impurities. Such behavior is seen in our samples at all temperatures investigated. Figures 4.24 and 4.25 show log-log plots of the paramagnetic rate at $T = 147 \, K$ and $T = 294 \, K$, respectively, as a function of Gd concentration for various samples with different hydrogen concentrations. Both at low temperature (rigid lattice) and high temperature (motional narrowing), a
Figure 4.24 Logarithm of the Gd-induced proton relaxation rate $R_{1p}$ versus logarithm of Gd concentration $y$ in $La_{1-x}Gd_xH_2$ at $T = 147$ K measured at 40 MHz. The solid lines are least-squares fits.
Figure 4.25 Logarithm of the Gd-induced proton relaxation rate $R_{1p}$ versus logarithm of Gd concentration $y$ in $La_{1-x}Gd_xH_x$ at $T = 294$ K measured at 40 MHz. The solid lines are least-squares fits.
linear relation between $R_{1p}$ and the impurity concentration $y$ is observed within experimental uncertainty, indicating that the Gd$^{3+}$ ions are randomly distributed in these samples. 

Figure 4.26 shows a plot of $R_{1p}$ versus Gd concentration at $T = 147$ K for LaH$_x$, $x = 2.5, 2.6, 2.7$ and $2.8$. For each sample the straight line passes through the origin. This indicates that the impurity contents determined by the mass spectrometric analysis are quite reliable.

Figure 4.27 shows a composite plot of the 25 ppm Gd-induced $R_{1p}$ on the logarithmic scale versus $1000/T$ in lanthanum hydrides. In common with the pure samples, two proton resonances with different spin-lattice relaxation times are observed in the Gd-doped LaH$_x$ for $x \geq 2.5$ over temperature ranges essentially the same as those in pure samples. For clarity, only the high-temperature component of $R_{1p}$ is shown in the figure. Contrarily, LaH$_{2.00}$ and LaH$_{2.35}$ show only a single $T_1$ for all temperatures. In particular, for LaH$_{2.35}$ good coverage of the temperature region of $R_{1p}$ showing different regimes was obtained, so it is a good system illustrating the behavior of the Gd$^{3+}$-induced relaxation rate $R_{1p}$, and we discuss it first in greater detail.
Figure 4.26 Composite plot of the Gd-induced proton relaxation rate $R_{1p}$ versus Gd concentration $y$ in $\text{La}_{1-x}\text{Gd}_x\text{H}_x$ at $T = 147$ K measured at 40 MHz. The lines are least-squares fits.
Figure 4.27 Composite plot of the 25 ppm Gd-induced proton spin-lattice relaxation rate $R_{1p}$ at 40 MHz versus reciprocal temperature (1000/T) for a series of Gd-doped lanthanum hydride samples LaH$_x$. 
2. $R_{1p}$ in LaH$_2$.35 + 53 ppm Gd

As shown in Figure 4.28, the main features of the temperature-dependent $R_{1p}$ are that for temperature below 227 K ($10^3/T > 4.4$) $R_{1p}$ is characterized by a very weak temperature dependence, while at higher temperatures $R_{1p}$ shows a very strong temperature dependence up to ~350 K ($10^3/T \approx 2.9$) and above 350 K a weaker but still pronounced temperature dependence. The dipolar interaction between the proton and Gd$^{3+}$ ion spins combined with both spin and atomic diffusion has been discussed in Chapter II, and we can now identify the different regimes described there as the spin-diffusion, slow atomic-diffusion and fast atomic-diffusion regimes which are well defined in this system.

i. Fast atomic diffusion regime

Quantitatively, $R_{1p}$ is expected to behave at high temperatures as

$$R_{1p} = \frac{(4\pi/3)NC}{a_1^3}$$

(4-20)

where $N$ is the impurity concentration per unit volume, $C$ is the strength of the impurity-proton dipolar interaction and $a_1$ is the distance of closest approach of a proton to the Gd$^{3+}$ ion. In the case of fcc lanthanum hydrides, $N = 4X/a_0^3$ and $a_1 = (\sqrt{3}/4)a_0$ where $a_0$ is the lattice constant and $X$ is the number of impurity ions per metal atom. This expression is Richards' extension to the fast atomic diffusion regime of the impurity-induced relaxation rate derived by Rorschach for fast spin diffusion as mentioned in Section B of Chapter II. The
Figure 4.28 Comparison of the experimental $R_{1P}$ values for LaH$_{2.35}$ + 53 ppm Gd with the predictions of Eq. 2-34. For the parameters used in this equation, see text.
interaction strength $C$ is given by

$$C = (2/5) \gamma_p^2 \gamma_n^2 \hbar^2 J(J+1) [\tau_1^*/(1+\omega_2^2 \tau_1^2)]$$  \hspace{1cm} (4-21)$$

where $\gamma_n$ and $\omega$ are the proton gyromagnetic ratio and Larmor frequency, respectively, and $J$ and $\gamma_p$ are the angular momentum and gyromagnetic ratio of the Gd$^{3+}$ ion, respectively. At high temperatures where the hydrogen diffusion becomes significant, the correlation time for the fluctuation of the interaction with an impurity ion is

$$\tau_1^* = 1/[1/\tau_1 + 1/\tau_0]$$  \hspace{1cm} (4-22)$$

with $\tau_1 = \text{spin-lattice relaxation time of the Gd}^{3+} \text{ ion and } \tau_0 = \text{mean dwell time for hydrogen hopping}$. Since as will be seen, $\tau_1 \ll \tau_0$ even at the highest temperature investigated, we have $\tau_1^* \approx \tau_1$. With $J = S = 7/2$ and $\gamma_p = g_p \mu_B / \hbar = 1.76 \times 10^7 \text{ Hz/Oe}$ ($g_p = 2.0$) for the Gd$^{3+}$ ion, Equation 4-21 can be written as (in s$^{-1}$ cm$^{-6}$)

$$C = 1.55 \times 10^{-3} \left[ \tau_1 / (1+\omega_2^2 \tau_1^2) \right].$$  \hspace{1cm} (4-23)$$

Furthermore, at 40 MHz the condition $\omega_2^2 \tau_1^2 \ll 1$ is well satisfied at high temperatures, so Equation 4-23 reduces to

$$C = 1.55 \times 10^{-3} \tau_1 \text{s}^{-1} \text{ cm}^{-6}.$$  \hspace{1cm} (4-24)$$

Using this result together with $N = 1.18 \times 10^{18} \text{ cm}^{-3}$ for 53 ppm Gd impurity, Equation 4-20 can be written as

$$R_{1,P} = 5.2 \times 10^{11} \tau_1 \text{s}^{-1}.$$  \hspace{1cm} (4-25)$$

In Figure 4.29 the relaxation rate $R_{1,P}$ is plotted against the temperature on log-log scales. It can be seen that the experimental data follow a relatively good linear relation
corresponding to an average dependence on temperature of the form $R_{1p} = 3.99 \times 10^3 T^{-0.80} s^{-1}$. According to Equation 4-25, this yields the dependence $\tau_1 = 7.6 \times 10^{-9} T^{-0.80} s$. Since the value of $\tau_1$ is somewhat too small, the phonon process is not considered to be a predominant relaxation mechanism. Among the proposed ion relaxation mechanisms, the $T^{-1}$ temperature dependence is predicted for the conduction-electron contribution. No direct measurements of $\tau_1$ in this temperature range for Gd$^{3+}$ in LaH$_2$ are available for comparison with our results, however, from the order of magnitude and the temperature dependence of $\tau_1$, it is not unreasonable to assume a Korringa process predominating in the paramagnetic-impurity relaxation. The discrepancy between the $T^{-0.80}$ and $T^{-1}$ temperature dependences may be due to the uncertainty in the determination of the slope of the high-temperature curve in Figure 4.29 because there are not enough data points.

Assuming a Korringa relation, the average value of the Korringa product obtained from four experimental $R_{1p}$ data points at highest temperatures measured is

$$\tau_1 T = 2.7 \times 10^{-8} sK.$$  \hspace{1cm} (4-26)

Then Equation 4-24 becomes

$$C = 4.19 \times 10^{-38} T^{-1} s^{-1} cm^{-6}. \hspace{1cm} (4-27)$$
ii. Slow atomic diffusion regime

At the peak of the $R_{1p}$ versus $1000/T$ curve (Figure 4.28), $T \approx 350$ K ($1000/T \approx 2.9$), the transition from the fast atomic diffusion regime to the slow atomic diffusion regime occurs. The transition is characterized by $\tau_0 = \tau(a_1)$, where $\tau(a_1)$ is the direct relaxation time of a proton located at the closest distance $a_1$ from the impurity ion. The atomic diffusion becomes very effective in transporting the proton magnetization to a region where the impurity ion is active. Therefore the relaxation rate $R_{1p}$ reflects a temperature dependence related to the activation energy of the thermally activated hydrogen diffusion. The relaxation rate in this temperature region can be approximated by $R_{1p} = (8\pi/3)NC_1^1/4D_a^{3/4}$ (Equation 2-31).

For LaH$_{2.33}$ + 53 ppm Gd, using the parameters discussed earlier and the temperature dependence of $C$ in Equation 4-27, the relaxation rate can be expressed as

$$R_{1p} = 7.95 \times 10^8 \times (10^3/T)^{1/4} \times D_a^{3/4} \tag{4-28}$$

where the atomic diffusion coefficient $D_a = D_0 \exp(-E_a/k_BT)$.

From the experimental $R_{1p}$ data the temperature dependence of $D_a$ is found to be (in cm$^2$/s$^{-1}$)

$$D_a = 1.52 \times 10^{-5}\exp(-0.34 \text{ eV/k}_B T). \tag{4-29}$$

The activation energy $E_a = 0.34$ eV/atom is in excellent agreement with the value 0.35 eV/atom obtained from the hydrogen dwell time $\tau_0$ in pure LaH$_{2.33}$. The prefactor $D_0 = (f_r \langle \xi^2 \rangle)/(6 \tau_0) = 1.52 \times 10^{-5}$ cm$^2$/sec. If we take $f_r = 1$ and
assume that the jump between nearest-neighbor interstitial T-O sites is representative of the various hydrogen jumps that can occur, then \( \lambda = (\sqrt{3}/4)a_o = 2.45 \) Å. We find that \( \tau_{0} = 6.6 \times 10^{-12} \) s which is larger than that obtained from the \( \tau_{1d} \) data in pure LaH\(_2\) by a factor of about 10. A similar situation was also found in the Gd-doped yttrium dihydride\(^7\). This discrepancy may indicate that the dwell time \( \tau_0 \) for hydrogen close to the Gd\(^{3+} \) ions differs from that appropriate to hydrogen far from the ions. Other possible sources for this discrepancy include the assumed jump length \( \lambda \) and the determination of the hydrogen dwell time \( \tau_0 \). The preexponential dwell time \( \tau_{0} \) determined using the BPP theory is not without uncertainty and is relatively insensitive to the microscopic details of the hydrogen motion. All these factors may combine in causing this discrepancy and therefore it should not be regarded as resulting from a failure of the method.

Taking

\[
\tau_0 = 6.6 \times 10^{-12} \exp(0.34 \text{ eV}/k_B T) \text{ s,} \tag{4-30}
\]

the condition \( \tau_0 \gg \tau_1 \) is well satisfied over the temperature range investigated. Equation 4-30 also yields a predicted temperature of about 330 K for the transition from slow to fast atomic diffusion regime which occurs when \( \tau_0 = a_1^6/C \). This temperature is satisfactorily close to the observed transition temperature. The transition between the two
regimes is achieved smoothly by the changing ratio of the Bessel functions in Equation 2-34. Figure 4.28 shows the results of the calculation made using the temperature dependencies of $\tau_1$ in Equation 4-26 and $\tau_0$ in Equation 4-30, together with the experimental $R_{1p}$ as a function of the reciprocal temperature.

**iii. Spin diffusion regime** Since hydrogen is essentially immobile at low temperatures, the only way to transport nuclear magnetization from regions far from a Gd$^{3+}$ ion is via spin diffusion. The transition to spin diffusion occurs when $D_s \sim D_a$, or equivalently $T_s \sim T_0$. The observed relaxation rate is jointly controlled by the direct relaxation rate near an impurity ion and by the spin diffusion rate and can be described by Equation 2-28,

$$R_{1p} = 8nND_s \beta \left[ \frac{\Gamma(3/4)}{\Gamma(1/4)} \right] \left[ \frac{1/4}{1/4} \right] \left[ \frac{13/4}{1-3/4} \right].$$

The temperature dependence of the relaxation rate $R_{1p}$ is the result of the variation of $\beta$ and $\delta$ with temperature, the former through the quantity $C$ which depends on the variable $\tau_1$ (Equation 2-26) and the latter through the quantities $\beta$ and $b$ which depends on both variables $\tau_1$ and $B(x)$ (Equations 2-29 and 2-30). The spin diffusion coefficient is essentially temperature independent.

Using the definition of the pseudopotential radius, $\beta = (C/D_s)^{1/4}$, Equation 2-28 can be rewritten as
\[ R_{1p} = 8nNC^{1/4} \frac{D_{s}^{9/4}}{\left[ \Gamma(3/4)/\Gamma(1/4) \right]} \frac{\left[ I_{3/4}(\delta)/I_{-3/4}(\delta) \right]}{I_{-3/4}(\delta)} \]  

(4-31)

As will be discussed later, the parameter \( \delta = \beta^2/(2b^2) \) is insensitive to temperature in the temperature range investigated here, and hence the temperature dependence is dominated by that of \( C_{r}^{1/4} \). Even though \( R_{1p} \) in the spin diffusion regime is only weakly temperature dependent, it does increase as the temperature decreases. Since from Equation 4-23, \( C \propto \tau_1/(1+\omega_0^2 \tau_1^2) \), it appears that \( R_{1p} \) should continue to increase until a temperature at which \( \omega_0 \tau_1 = 1 \) is reached. Following this maximum the rate will then decrease with decreasing temperature. If the relation \( \tau_1 T = 2.7 \times 10^{-8} \) s K (Equation 4-26) holds down to very low temperature, this maximum in \( R_{1p} \) observed at 40 MHz is expected to occur at 6.8 K, a temperature too low to permit effective observation.

However, this behavior of \( R_{1p} \) has been observed for some of the samples with higher hydrogen concentrations in this work. Thus, \( \tau_1 \) can be determined at the temperature at which the maximum in \( R_{1p} \) occurs in the spin diffusion regime, and the shape of the peak enables us to estimate the temperature dependence of \( \tau_1 \).

3. \( R_{1p} \) in the fast atomic diffusion regime

From Figure 4.27 we can see that the main features of \( R_{1p} \) observed in the case of \( \text{LaH}_2.35 \) can also be seen in samples
with different hydrogen concentrations. However, the maximum Gd$^{3+}$-induced rate, $R_{1p, max}$, in LaH$_{3.0}$ is more than 80 times that in LaH$_{2.0}$. Furthermore, the sharply peaked character of $R_{1p}$ in the trihydrides stands in contrast to its flat character in the dihydrides. Qualitatively, these features indicate a marked slowing down of the Gd$^{3+}$ ion spin-lattice relaxation rate accompanied by a changeover from conduction electron to phonon dominated relaxation of the ion spin.

At high temperatures $R_{1p}$ is given by Equation 4-20,

$$R_{1p} = \frac{4n}{3} NC/a_1^3$$  \hspace{1cm} (4-20)

with

$$C = \frac{2}{5} \gamma_p^2 \gamma_e^2 M^2 J(J+1)\tau_1^*,$$  \hspace{1cm} (4-21)

assuming that $\omega^2 \tau_1^{*2} \ll 1$. Each term has its usual meaning as described in Section B.2 of this chapter. In the light of these relationships, the high temperature data of $R_{1p}$ should give us information on the nature of the interaction involved in $\tau_1$.

In Equation 4-21 the correlation time for the interaction between the proton and the Gd$^{3+}$ ion moments is

$$\tau_1^* = \frac{1}{(1/\tau_1 + 1/\tau_0)}.$$  \hspace{1cm} (4-22)

Since $\tau_1 \ll \tau_0$ in the dihydride phase, we have $\tau_1^* = \tau_1$. But, as discussed in Section A.3 of Chapter IV, an increase in hydrogen concentration in lanthanum hydrides increases the proton jump frequency, or equivalently decreases the dwell time $\tau_0$. On the other hand, the changeover from metal to nonmetal slows down the Gd$^{3+}$ ion relaxation rate. Therefore,
1/\tau_0\ may\ become\ important\ in\ contributing\ to\ 1/\tau_1^*\ for\ the\ trihydride\ phase.\ However,\ it\ can\ be\ shown\ that\ 1/\tau_0\ does\ not\ overwhelm\ 1/\tau_1\ in\ the\ temperature\ range\ investigated\ here.\ As\ a\ check\ we\ choose\ the\ case\ of\ LaH_{2.80}\ which\ exhibits\ only\ a\ single\ phase\ in\ the\ entire\ fast\ atomic\ diffusion\ regime.\ At\ T = 500\ K,\ the\ 53\ ppm\ Gd-induced\ relaxation\ rate\ \( R_{1P} = 34s^{-1} \) and\ this\ gives\ \( \tau_1^* = 6.6 \times 10^{-11}s \) from\ Equations\ 4-20\ and\ 4-21.\ If\ we\ take\ the\ expression\ for\ \( \tau_0 \) obtained\ from\ the\ high-temperature\ phase\ in\ pure\ LaH_{2.80},\ \( \tau_0 = 1.5 \times 10^{-10}s \) at\ T = 500\ K\ which\ is\ still\ a\ factor\ of\ 20\ larger\ than\ \( \tau_1^* \).\ Furthermore,\ hydrogen\ diffusion\ in\ the\ vicinity\ of\ the\ impurity\ ion\ seems\ to\ be\ slower\ than\ that\ in\ the\ bulk\ (as\ observed\ in\ the\ case\ of\ LaH_{2.35}),\ and\ this\ makes\ the\ relevant\ \( \tau_0 \)\ longer\ than\ that\ in\ the\ pure\ sample.\ In\ view\ of\ this\ we\ assume\ that\ \( \tau_1^* \approx \tau_1 \)\ for\ preliminary\ discussion.\ We\ then\ expect\ that\ \( R_{1P} \approx \tau_1 \)\ from\ Equation\ 4-20\ and\ write\ finally,

\[
R_{1P} = \frac{[(8\pi/15)\eta y P^2 \gamma_0^2 M^2 J(J+1)]/a_1^2]}{\tau_1} \quad (4-32)
\]

which\ will\ reflect\ the\ temperature\ dependence\ of\ \( \tau_1 \).

The\ temperature\ dependence\ of\ \( R_{1P} \)\ can\ be\ determined\ by\ plotting\ \( \log R_{1P} \)\ versus\ \( \log T \).\ Figures\ 4.29\ to\ 4.35\ show\ such\ plots\ of\ \( R_{1P} \)\ data\ for\ a\ series\ of\ LaH_x\ +\ Gd\ samples.\ The\ high-temperature\ portions\ of\ these\ plots\ show\ reasonable\ straight-line\ behavior.\ By\ using\ the\ known\ values\ of\ the\ constants\ in\ Equation\ 4-32,\ the\ temperature\ dependence\ of\ \( \tau_1 \)\ for\ a\ series\ of\ LaH_x\ can\ be\ deduced.\ The\ results,\ together\ with\ \( \tau_1 \)\ values
Figure 4.29  Logarithm of the 53 ppm Gd-induced proton spin-lattice relaxation rate, log $R_{1p}$, against logarithm of temperature for LaH$_{2.35}$ in the fast atomic diffusion regime. The solid line is the best fit to the straight-line portion of the data.
Figure 4.30 Logarithm of the 300 ppm Gd-induced proton spin-lattice relaxation rate, log $R_{1p}$, against logarithm of temperature for LaH$_{2.50}$ in the fast atomic diffusion regime. The solid line is the best fit to the straight-line portion of the data.
LaH$_{2.60}$ + 25 ppm Gd at 40 MHz

$R_1p = 6.24 \times 10^4 \ T^{-1.34} \ \text{s}^{-1}$

Figure 4.31  Logarithm of the 25 ppm Gd-induced proton spin-lattice relaxation rate, log $R_1p$, against logarithm of temperature for LaH$_{2.60}$ in the fast atomic diffusion regime. The solid line is the best fit to the straight-line portion of the data.
Figure 4.32 Logarithm of the 53 ppm Gd-induced proton spin-lattice relaxation rate, log $R_{1p}$, against logarithm of temperature for LaH$_{2.70}$ in the fast atomic diffusion regime. The solid line is the best fit to the straight-line portion of the data.
LaH$_{2.80}$ + 53 ppm Gd at 40 MHz

Figure 4.33 Logarithm of the 53 ppm Gd-induced proton spin-lattice relaxation rate, log $R_{1p}$, against logarithm of temperature for LaH$_{2.80}$ in the fast atomic diffusion regime. The solid line is the best fit to the straight-line portion of the data.
Figure 4.34 Logarithm of the 53 ppm Gd-induced proton spin-lattice relaxation rate, log $R_{1p}$, against logarithm of temperature for $\text{LaH}_2.90$ in the fast atomic diffusion regime. The solid line is the best fit to the straight-line portion of the data.

$R_{1p} = 3.55 \times 10^{14} T^{-4.83} \text{s}^{-1}$
Figure 4.35 Logarithm of the 53 ppm Gd-induced proton spin-lattice relaxation rate, log $R_{1P}$, against logarithm of temperature for LaH$_{3.00}$ in the fast atomic diffusion regime. The solid line is the best fit to the straight-line portion of the data.
at $T = 350$ K, are listed in Table 4-3. For samples with $[H]/[La] \geq 2.7$, the bend in the curve near the high-temperature end may possibly be attributed to a change in the relaxation process of the paramagnetic ions.

Several features of these results are significant. First of all, at a typical temperature $T = 350$ K, the Gd$^{3+}$ ion spin-lattice relaxation time increases with increasing $[H]/[La]$ composition. This fact clearly indicates that the Gd$^{3+}$ ion spin-lattice relaxation rate slows down as the host LaH$_x$ becomes less metallic. Secondly, the temperature dependence of $\tau_i$ behaves very differently for $x < 2.7$ and $x > 2.7$. It can be seen from Table 4-3 that $\tau_i \propto T^{-n}$ with $n \approx 1$ for $x < 2.7$ whereas $n \approx 5$ for $x > 2.7$.

As discussed in Chapter II, two mechanisms are important to the process of Gd$^{3+}$ ion relaxation in lanthanum hydrides; namely the conduction-electron contribution $(\tau_i)_{ei}$ and the phonon contribution $(\tau_i)_{ph}$. It is believed that $(\tau_i)_{ei}$ follows Korringa-like behavior (i.e. $\propto T^{-1}$). From the temperature dependence of $\tau_i$ in LaH$_{2.35}$, LaH$_{2.50}$ and LaH$_{2.60}$, we find that the ion relaxation process is dominated by the conduction-electron contribution. Since the phonon contribution is the result of changes in the interaction between the crystalline electric field and orbital moment induced by lattice vibrations, and since Gd$^{3+}$ is an S-state ion (4f shell half filled and total spin $J = S = 7/2$) thus $L =$
Table 4-3. Summary of the Gd\(^{3+}\) ion spin-lattice relaxation time behavior in the high temperature region for LaH\(_x\) + Gd obtained using Equation 4-32

<table>
<thead>
<tr>
<th>(x = [H]/[La])</th>
<th>(\tau_1) (sec)</th>
<th>(\tau_1) (350 K) (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.35</td>
<td>(7.6 \times 10^{-9} \ T^{-0.80})</td>
<td>(7.0 \times 10^{-11})</td>
</tr>
<tr>
<td>2.50</td>
<td>(7.7 \times 10^{-9} \ T^{-0.80})</td>
<td>(7.1 \times 10^{-11})</td>
</tr>
<tr>
<td>2.60</td>
<td>(2.5 \times 10^{-7} \ T^{-1.34})</td>
<td>(9.7 \times 10^{-11})</td>
</tr>
<tr>
<td>2.70</td>
<td>(2.4 \times 10^{-1} \ T^{-3.66})</td>
<td>(1.2 \times 10^{-10})</td>
</tr>
<tr>
<td>2.80</td>
<td>(1.6 \times 10^{3} \ T^{-5.08})</td>
<td>(1.9 \times 10^{-10})</td>
</tr>
<tr>
<td>2.90</td>
<td>(6.8 \times 10^{3} \ T^{-4.83})</td>
<td>(3.5 \times 10^{-10})</td>
</tr>
<tr>
<td>3.00</td>
<td>(2.1 \times 10^{3} \ T^{-4.95})</td>
<td>(5.4 \times 10^{-10})</td>
</tr>
</tbody>
</table>
0, the phonon contribution may be neglected to first order in the metallic hydrides. Also, the electron screening of the electric field fluctuations due to phonons drastically reduces the phonon contribution in these samples.

For the nonmetallic samples the phonon contribution becomes dominant, especially at high temperatures, and as a result the temperature dependence of $\tau_1$ is much stronger. This can be seen in the cases of $\text{LaH}_2.70$, $\text{LaH}_2.80$, $\text{LaH}_2.90$ and $\text{LaH}_3.00$. The $T^{-5}$ dependence of $\tau_1$ may arise from two-phonon relaxation processes involving excited states within the $S_{7/2}$ multiplet. For $\text{LaH}_3.00$ we have that $\tau_1^{-1} = 4.8 \times 10^{-4} T^{-5} s^{-1}$ which may be compared with the behavior of $S$-state rare-earth ions in insulating crystals. The relaxation rate of $\text{Gd}^{3+}$ ions in tetragonal sites in $\text{CaF}_2$ was measured directly by Bierig et al. Their data were obtained using the pulsed saturation method at 9.6 GHz. It was found that the temperature dependence of the $\text{Gd}^{3+}$ ion spin-lattice relaxation rate could be fit by $\tau_1^{-1} = 9.1 \times 10^4 T^{1/2} + 2.5 \times 10^{-4} T^5 s^{-1}$. The relaxation of divalent europium ions $\text{Eu}^{2+}$ in $\text{CaF}_2$ by Huang yielded $\tau_1^{-1} = 12 T + 5.3 \times 10^{-4} T^5 s^{-1}$. At high temperatures, $\tau_1^{-1}$ is dominated by the $T^5$ term since the term in $T$ or $T^{1/2}$ is only significant at temperatures below ~20 K. The $T^5$ dependence observed for $\text{Gd}^{3+}$ in $\text{LaH}_3.00$ is very close to these results, especially for $\text{Eu}^{2+}$ in $\text{CaF}_2$ in which $\text{Eu}^{2+}$ is also in the cubic site. Thus, from the temperature dependence of $\tau_1$
shown in Table 4-3, we draw the following conclusion: At high temperatures, LaH$_x$ is a metallic host for $x \leq 2.6$ and an insulating host for $x > 2.7$.

4. $R_{ip}$ in the spin diffusion regime

In order to investigate the behavior of the ion spin-lattice relaxation time $\tau_1$ at low temperatures, the proton spin-lattice relaxation time $T_1$ was measured on a series of LaH$_x$ ($x = 2.50, 2.61, 2.69, 2.80$ and $2.87$) samples doped with $300$ ppm Gd over the temperature range $7$-$150$ K. At low temperatures where hydrogen diffusion is insignificant, the measured proton spin-lattice relaxation rate $R_1$ is primarily due to the paramagnetic ion contribution $R_{ip}$. For example, at $T = 147$ K the measured relaxation rate in LaH$_{2.80}$ + $300$ ppm Gd at $40$ MHz is $11.14$ s$^{-1}$ while that in the pure sample is only $0.26$ s$^{-1}$. Therefore, it is an excellent approximation to consider the measured $R_1$ as $R_{ip}$. The relaxation rate $R_{ip}$ in the spin diffusion regime given by Rorschach has been discussed in Chapter II (Equation 2-28) and Chapter IV (Equation 4-31), and is repeated here for convenience,

$$R_{ip} = 8nNC_1^{1/4}D_s^{3/4}\left[\Gamma(3/4)/\Gamma(1/4)\right]$$

$$\left[I_{3/4}(5)/I_{-3/4}(5)\right].$$

(4-31)

The meaning of each term was described earlier. As discussed in Section B.2 of Chapter IV for the case of LaH$_{2.35}$ + $53$ ppm Gd, the temperature dependence of $R_{ip}$ mainly reflects the
variation of $\tau_1$ with temperature through the relation, $C \propto \tau_1/(1+\omega^2\tau_1^2)$, and a maximum in $R_{1p}$ is expected to occur at the temperature where $\omega \tau_1 = 1$.

Figure 4.36 shows the log-log plot of the paramagnetic relaxation rate as a function of temperature for LaH$_{2.80}$ + 300 ppm Gd at 40 MHz. For temperatures below ~160 K the spin diffusion regime is reached, and $R_{1p}$ becomes weakly temperature dependent, increasing slowly with decreasing temperature. The maximum in $R_{1p}$ is still not seen at $T = 10$ K. This fact suggests that the product $\tau_1 T < 4.0 \times 10^{-8}$ s K, if $\tau_1$ follows Korringa-type behavior in LaH$_{2.80}$. For 40 K < $T$ < 150 K, the curve in Figure 4.36 follows a relatively good linear relation corresponding to a temperature dependence of the form $R_{1p} \propto T^{-0.30}$. If $\tau_1$ obeys the Korringa relation, $\tau_1 T = \text{constant}$, the theory predicts the relation $R_{1p} \propto T^{-0.23}$ in the slow spin diffusion regime at temperatures well above that of $R_{1p,\text{max}}$. A measurement of $R_{1p}$ at 12.2 MHz was also made in the low temperature range, giving good qualitative agreement reflecting the frequency dependence of $C^{1/4}[\tau_1/(1+\omega^2\tau_1^2)]^{1/4}$ in the vicinity of the maximum.

For LaH$_{2.61}$ + 300 ppm Gd a weak hump near $T = 15$ K appears, as shown in Figure 4.37. On the basis of earlier comments, it can be seen that this corresponds to the condition $\omega \tau_1 = 1$. Since the measurements were made with the proton Larmor frequency $f = 40$ MHz, the spin-lattice
Figure 4.36 Temperature dependence of the Gd-induced proton relaxation rate $R_{1p}$ in LaH$_{2.50}$ + 300 ppm Gd at 40 MHz.
Figure 4.37 Temperature dependence of the Gd-induced proton relaxation rate $R_{1p}$ in $\text{LaH}_{2.61} + 300$ ppm Gd at 40 MHz.
relaxation time $t_1$ of the Gd$^{3+}$ spins in the sample at $T = 15$ K is $4.0 \times 10^{-9}$ s. This value is five orders of magnitude shorter than that of Gd$^{3+}$ ions in CaF$_2$ and six orders of magnitude shorter than that of Eu$^{2+}$ ions in CaF$_2$. Moreover, the temperature dependence of $R_{1p}$ could be somewhat too weak if there were a significant ion relaxation rate via phonons. Therefore, we suggest that the Gd$^{3+}$ ion spin is relaxed predominantly by conduction electrons in this hydrogen concentration range. The value of $t_1$ at $T = 15$ K yields the Korringa product $t_1 T = 6.0 \times 10^{-8}$ s K. If this value is taken over the entire temperature range covered in the spin diffusion regime, values of $R_{1p}$ can be calculated from Equation 4-31. First of all, a value of the spin diffusion coefficient is required. If we take the expression given by Lowe and Gade (Equation 2-24), the value obtained is $D_s = 4.0 \times 10^{-12}$ cm$^2$s$^{-1}$. For the Gd$^{3+}$ ion, $C = 1.55 \times 10^{-20}$ $[t_1/(1+\omega^2 t_1^2)]$ (see Equation 4-23) where $t_1 = 6 \times 10^{-8}/T$ (in s). Using this expression the pseudopotential radius can be calculated, since $\beta = (C/D_s)^{1/4}$ (Equation 2-26). The spin diffusion barrier radius $b$ at the field $H_0 = 9395$ G corresponding to the proton resonance at 40 MHz can be deduced from Equations 2-29 and 2-30. Then we have the following values at some specific temperatures (Table 4-4), for the case of LaH$_2.61$.

From these parameters it is seen that the situation is
Table 4-4. Values of $\beta$, $b$, $\delta$, and $I_{3/4}(\delta)/I_{-3/4}(\delta)$ for LaH$_{2.61}$ + 300 ppm Gd calculated using the theory outlined in Sec. B.3. of Chapter II.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\beta$ (Å)</th>
<th>b (Å)</th>
<th>$\delta = \beta^2/(2b^2)$</th>
<th>$I_{3/4}(\delta)/I_{-3/4}(\delta)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>12.28</td>
<td>9.64</td>
<td>0.811</td>
<td>0.66</td>
</tr>
<tr>
<td>50</td>
<td>14.37</td>
<td>11.1</td>
<td>0.846</td>
<td>0.68</td>
</tr>
<tr>
<td>20</td>
<td>16.50</td>
<td>13.5</td>
<td>0.745</td>
<td>0.61</td>
</tr>
<tr>
<td>15</td>
<td>16.70</td>
<td>14.4</td>
<td>0.671</td>
<td>0.56</td>
</tr>
<tr>
<td>10</td>
<td>16.33</td>
<td>15.9</td>
<td>0.527</td>
<td>0.44</td>
</tr>
</tbody>
</table>
intermediate between the fast and slow spin-diffusion regimes. It should be noted that Equation 2-24 is just an order-of-magnitude expression for $D_a$. However, since both $\beta$ and $b$ increase slowly with decreasing temperature, the ratio $I_3/4(\delta)/I_{-3/4}(\delta)$ is only weakly temperature dependent. If we ignore the small variation of $I_3/4(\delta)/I_{-3/4}(\delta)$ with temperature and take its value calculated at the temperature of the maximum in $R_{iP}$, the expression for $R_{iP}$ (Equation 4-31) may be reduced to

$$R_{iP} = 3.24 \times 10^3 \left[ \frac{\tau_1}{1 + \omega^2 \tau_1^2} \right]^{1/4} \text{s}^{-1}. \quad (4-33)$$

Figure 4.35 shows the results of the calculation, assuming that $\tau_1 T = 6 \times 10^{-8} \text{s} \text{K}$, together with the experimental $R_{iP}$ as a function of temperature $T$. Although the fit is not perfect, it reveals that there is no indication of a significant phonon contribution to the ion relaxation time $\tau_1$.

The behavior of $R_{iP}$ for LaH$_2$ + 300 ppm Gd ($x = 2.69, 2.80$ and $2.87$) in the spin diffusion regime is similar to that for LaH$_{2.41} + 300$ ppm Gd. The principal difference, however, is the shift of the temperatures of $R_{iP, max}$ to higher temperatures with increasing hydrogen concentration (Figures 4.39, 4.40 and 4.41). Since the temperature dependence of $R_{iP}$ is so weak, it is unlikely that a strong temperature dependence of $\tau_1$ is involved. Therefore, we assume a Korringa-type $\tau_1$ at low temperatures. Again, from the value of $\tau_1$ determined at the temperature where $R_{iP, max}$ occurs, the
Figure 4.38 Comparison of the experimental $R_{1p}$ values for LaH$_{2.61}$ + 300 ppm Gd with the predictions of Eq. 4-33 (the broken line) in the spin diffusion regime.
Figure 4.39 Temperature dependence of the 300 ppm Gd-induced proton relaxation rate $R_{1P}$ at 40 MHz for Gd-doped LaH$_{2.69}$ in the spin diffusion regime. For the parameters used in the calculations, see text.
Figure 4.40 Temperature dependence of the 300 ppm Gd-induced proton relaxation rate $R_{1p}$ at 40 MHz for Gd-doped $\text{LaH}_2.80$ in the spin diffusion regime. For the parameters used in the calculations, see text.
Figure 4.41 Temperature dependence of the 300 ppm Gd-induced proton relaxation rate $R_1p$ at 40 MHz for Gd-doped LaH$_{2.87}$ in the spin diffusion regime. For the parameters used in the calculations, see text.
product $\tau_1 T$ can be obtained. The values are $\tau_1 T = 9.6 \times 10^{-8}$ s K and $1.7 \times 10^{-7}$ s K for LaH$_2.69$ and LaH$_2.80$ doped with 300 ppm Gd, respectively. Following the argument given in the case of LaH$_2.67 + 300$ ppm Gd, the expression for the relaxation rate (Equation 4-31) can be written as

$$R_{1p} = 3.55 \times 10^3 \left[ \frac{\tau_1}{1 + \omega^2 \tau_1^2} \right]^{1/4} s^{-1}$$

(4-34)

with $\tau_1 T = 9.6 \times 10^{-8}$ s K for LaH$_2.69 + 300$ ppm Gd, and

$$R_{1p} = 3.8 \times 10^3 \left[ \frac{\tau_1}{1 + \omega^2 \tau_1^2} \right]^{1/4} s^{-1}$$

(4-35)

with $\tau_1 T = 1.7 \times 10^{-7}$ s K for LaH$_2.80 + 300$ ppm Gd. The results of the calculation are shown in Figures 4.39 and 4.40. The discrepancy can be reduced by taking into account the temperature dependence of the Bessel functions in Equation 4-31.

For LaH$_2.87 + 300$ ppm Gd it is found that $R_{1p,\text{max}}$ occurs at a temperature above 120 K, and its observation is hindered by the transition from the spin diffusion regime to the atomic diffusion regime. Thus a rigorous analysis of the data is not possible, but it should be pointed out that the temperature dependence of $\tau_1$ is not stronger than $T^{-1}$. If we again assume a Korringa-type $\tau_1$, the occurrence of $R_{1p,\text{max}}$ near $T \gtrsim 120$ K gives $\tau_1 T \gtrsim 4.8 \times 10^{-7}$ s K. Using this value and ignoring the temperature dependence of the Bessel functions, the calculated $R_{1p}$ is in good qualitative agreement with the data (see Figure 4.41).

To summarize the foregoing discussion we may say that the
shape of the peak of $R_{1p}$ in the spin diffusion regime indicates a Korringa-type $\tau_1$ for all LaH$_x$ + 300 ppm Gd samples ($x = 2.50, 2.61, 2.69, 2.80$ and $2.87$). In other words, the Gd$^{3+}$ ion relaxation rate is dominated by the conduction-electron contribution. This suggests that all the LaH$_x$ ($x \leq 2.87$) samples are metallic hosts in this temperature range. The temperature of $R_{1p,\text{max}}$ shifts consistently to higher temperatures with increasing hydrogen concentration. This feature reflects an increase in the value of the $\tau_1 T$ product as the host sample becomes less metallic. The values of $\tau_1 T$ obtained from $R_{1p,\text{max}}$ are summarized in Table 4.5.

Figure 4.42 shows $(\tau_1 T)^{-1/2}$ as a function of $x$, in which the curve is again the free-electron approximation fit at $x = 2.61$. The agreement is not so good as in Figure 4.12. It is possible that the effective exchange interaction parameter that determines the coupling between the electrons and the Gd ion is itself somewhat dependent on the hydrogen concentration$^{33}$, so that $(\tau_1 T)^{-1/2}$ is not just a function of $N(E_F)$.

Compared with the high-temperature behavior which shows that LaH$_x$ is metallic for $x \leq 2.60$ and insulating for $x \geq 2.70$, a temperature-dependent transition in electronic properties occurs in LaH$_x$ ($x = 2.70, 2.80$ and $2.87$). The transition temperature lies within the two-resonance region. Since in this temperature range $R_{1p}$ at 40 MHz is characterized
Table 4-5. The values of the product $\tau_1 T$ for Gd$^{3+}$ in LaH$_x$ determinated from the measured $R_1 p$ at the temperature of the maximum in the spin diffusion regime

<table>
<thead>
<tr>
<th>$x = [H]/[La]$</th>
<th>$\tau_1 T$ (s K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.50</td>
<td>$\leq 4.0 \times 10^{-8}$</td>
</tr>
<tr>
<td>2.61</td>
<td>$6.0 \times 10^{-8}$</td>
</tr>
<tr>
<td>2.69</td>
<td>$9.6 \times 10^{-8}$</td>
</tr>
<tr>
<td>2.80</td>
<td>$1.7 \times 10^{-7}$</td>
</tr>
<tr>
<td>2.87</td>
<td>$\geq 4.8 \times 10^{-7}$</td>
</tr>
</tbody>
</table>
Figure 4.42 Plot of \((\tau_1 T)^{-1/2}\) as a function of hydrogen concentration for Gd\(^{3+}\) in LaH\(_x\). The broken line shows a curve based on the free-electron density-of-states going as \((3 - x)^{1/3}\).
by the atomic diffusion coefficient $D_a$, the transition
temperature itself cannot be derived from the $R_{1p}$
measurements. At any rate, the behavior of the Gd$^{3+}$ ion
relaxation time in lanthanum hydrides found in this work is
compatible with electrical resistivity changes as a function
of hydrogen concentration and temperature. Resistivity
measurements using an indirect, Q-meter technique on LaH$_x$ ($x =$
2.70, 2.80, 2.90 and 2.93) have been undertaken in the Ames
Laboratory by Shinar et al.\textsuperscript{7,8}. For samples with $x =$ 2.70,
2.80 and 2.90, LaH$_x$ shows metallic behavior at low
temperatures and insulating behavior at high temperatures.
The transition temperature is around 250 K. For the sample of
nominal hydrogen concentration $x =$ 2.93, the behavior is
insulating-like at all temperatures.

From measurements of the proton $T_1$ both in the atomic
diffusion and spin diffusion regimes, we have obtained the
temperature dependence of the spin-lattice relaxation time $\tau_1$
of the Gd$^{3+}$ ions. We now wish to compare the values of $\tau_1$
obtained from high and low temperature ranges. Figures 4.43,
4.44 and 4.45 show the temperature dependence of $\tau_1$ for Gd$^{3+}$
in LaH$_x.6$, LaH$_x.7$ and LaH$_x.8$, respectively, as listed in
Tables 4-3 and 4-5. Although values of $\tau_1$ in the slow atomic
diffusion regime ($150 \text{ K} \sim 250 \text{ K}$) were not determined from the
measured $R_{1p}$ data, the reasonably good match between the two
sets of data indicates that $\tau_1$ is a monotonically decreasing
Figure 4.43 Spin-lattice relaxation time $\tau_1$ for Gd$^{3+}$ in LaH$_{2.6}$ obtained from measured $R_1$ data.
Figure 4.44 Spin-lattice relaxation time $\tau_1$ for Gd$^{3+}$ in LaH$_{2.7}$ obtained from measured $R_{1P}$ data.
Figure 4.45 Spin-lattice relaxation time $\tau_1$ for Gd$^{3+}$ in LaH$_{2.8}$ obtained from measured $R_{1P}$ data.
function of temperature as generally expected.

In the measurements of Guzzle and Mahendroo\textsuperscript{77}, the determinations of $\tau_i$ of rare-earth ions in CaF$_2$ were based on the prediction that a maximum in the $R_{1p}$-versus-temperature curve corresponding to the condition $\omega_0 \tau_i = 1$ occurs in the slow spin diffusion regime. This can also be applied in our cases, although the situation is intermediate between the fast and slow diffusion regimes, because $\tau_i$ is a monotonically decreasing function of temperature and the parameter $\delta = \beta^2/(2b^2)$ varies slowly in the vicinity of the maximum. The $\tau_i T$ values determined in this way should be relatively reliable. In the case of LaH$_2$.6, we have $\tau_i T = 6.0 \times 10^{-8}$ s K at low temperatures (Table 4-5) and $\tau_i = 2.5 \times 10^{-7}$ T$^{-1.34}$ s at high temperatures (Table 4-3). It should be remembered, however, that the correlation time $\tau_i^* \approx \tau_i$ was assumed in Equation 4-32 to obtain the latter expression. We now treat it more rigorously. From Equation 4-20, $\tau_i^*$ can be obtained, then we take $\tau_0$ from $T_{1d}$ for the pure LaH$_2$.6 sample. Since $\tau_i^*-1 = \tau_i^{-1} + \tau_0^{-1}$, allowance for $\tau_0$ leaves $\tau_i T = 3.8 \times 10^{-8}$ s K. This value is a little smaller than $6.0 \times 10^{-8}$ s K obtained at low temperatures. That is probably because of the difference between the local $\tau_0$ near the Gd$^{3+}$ ion and the bulk $\tau_0$ we used. It is also possible that the phonon relaxation becomes more important at high temperatures so that the determination of $\tau_i T$ becomes more ambiguous.
No direct measurements of $\tau_i$ for Gd$^{3+}$ in LaH$_x$ are available for comparison with these results, since $\tau_i$ is very short and direct measurements are difficult to make. However, electron-spin-resonance (ESR) measurements of Gd$^{3+}$ were made at 9.3 GHz on the same lanthanum hydride samples in the temperature range between 4 K and 300 K. It was anticipated that the temperature dependence of the resonance linewidth would correspond to the behavior of $\tau_i$. Unfortunately, the observed ESR spectra do not simply reflect a linewidth due to the relaxation time, but exhibit relatively complicated structure which may be attributed to the symmetry of the local environment of hydrogen atoms at the Gd$^{3+}$ sites. For Gd-doped LaH$_{2.92}$, the ESR spectrum is dominated by a large resonance line with a $g$-factor equal to $g = 1.93$. Its linewidth increases linearly with temperature. If we assume that this represents the lifetime broadening associated with the spin-lattice relaxation of the ion, we find that $\tau_i$ conforms to a Korringa relation, $\tau_i T = 2.5 \times 10^{-7}$ s K, at temperatures below 140 K. This yields coarse order-of-magnitude agreement with the result for LaH$_{2.87}$ (Table 4.5).
V. SUMMARY AND CONCLUSIONS

The temperature and concentration dependences of the NMR spin-lattice relaxation time $T_1$ of protons both in pure $\text{LaH}_2$ and in $\text{Gd}^{3+}$-doped $\text{LaH}_2$ have been measured over the temperature range 10-700 K. Some observations of the resonance line shape were also made over a limited temperature range.

For samples with $[\text{H}]/[\text{La}] < 2.5$, only a single $T_1$ appears at all temperatures investigated. The features of the $T_1$ curves are consistent with the predictions of the conventional Bloembergen-Purcell-Pound theory and show no trace of a second motional process or change in activation energy with temperature. For hydrogen concentration $x \geq 2.5$, two proton resonances having different $T_1$ values are observed to coexist over some temperature interval in the range 150 K to 270 K, depending on the hydrogen concentration. The origin of the two NMR signals is still not clearly understood.

The proton resonance second moments determined from the measured values of $T_1d_{\text{mm}}$ confirm that in the high-temperature phase nearly all tetrahedral sites are occupied and that the octahedral sites fill randomly. The activation energy and attempt frequency for hydrogen diffusion decrease significantly with increasing hydrogen concentration, supporting the interpretation, first advanced by Schreiber and
Cotts\textsuperscript{27}, that O-site occupation is responsible for this phenomenon.

In the dihydride phase, the spin-lattice relaxation rate $T_1^{-1}$ at low temperatures is dominated by the conduction electron contribution $T_{1e}^{-1}$, consistent with the metallic character of these hydrides. As $[\text{H}]/[\text{La}]$ increases, our determinations of $T_{1e}$ show a substantial decrease in $(T_{1e}T)^{-1/2}$ and therefore in the electronic density-of-states at the Fermi level $N(E_F)$. The behavior of $N(E_F)$ is in good agreement with expectations based on the free-electron approximation, that goes as $(3 - x)^{1/3}$, at least up to $[\text{H}]/[\text{La}] = 2.8$.

A primary goal of this work has been to obtain the temperature dependence of the correlation time $\tau_i$ of Gd impurity spin fluctuations from measurements of the proton spin-lattice relaxation time $T_1$ in Gd-doped LaH$_x$ samples. For small Gd concentrations, for which the interactions between the impurities can be neglected, $\tau_i$ is just the spin-lattice relaxation time of the Gd$^{3+}$ ions, and thereby also provides information on the electronic properties of the host lanthanum hydrides.

At low temperatures, in the spin diffusion regime, the $R_1 - T$ curve exhibits a maximum, corresponding to the maximum in the spectral density function of the ion spin fluctuations, for LaH$_x + 300$ ppm Gd up to a hydrogen concentration between
The temperature dependence of $\tau_i$ determined from the $R_{1P}$ data indicates conduction-electron relaxation of the Gd$^{3+}$ ion at these compositions and temperatures. The temperature of the peak in $R_{1P}$, and consequently the product $\tau_i T$, increases with increasing hydrogen composition, in qualitative agreement with the anticipated change in the electronic structure. At high temperature, in the fast atomic diffusion regime, we expected that $R_{1P} \propto \tau_i$. The measurements reveal a changeover from conduction electron ($\tau_i \propto T^{-1}$) to phonon ($\tau_i \propto T^{-3}$) dominated relaxation of the Gd$^{3+}$ spin as $[H]/[La]$ increases from 2.5 to 3.0.

In conclusion, the behavior of the spin-lattice relaxation time $\tau_i$ of the Gd$^{3+}$ ion in lanthanum hydrides shows that (a) these materials are metallic at all temperatures up to a hydrogen concentration $x \approx 2.7$, (b) they are at least weakly metallic at all $x$ values at temperatures below $150$ K, and (c) for $x > 2.7$ they are nonmetallic at temperatures above $250$ K.
VI. REFERENCES


VII. ACKNOWLEDGMENTS

It is with real appreciation that I acknowledge my indebtedness to my major professor, Dr. R. G. Barnes. I wish to thank him for his patient guidance and his effort in carefully reading and suggestions on this thesis.

I would like to thank Mr. D. R. Torgeson for the direct help and training I have received in NMR-spectrometer techniques. His knowledge in this field is to be respected.

Special thanks are due to Professor E. F. W. Seymour of the University of Warwick, England, for many fruitful discussions which have been most useful for the completion of this work.

I am indebted to B. J. Beaudry and N. Beymer of the Material Preparation Center of the Ames Laboratory for their careful preparation of the lanthanum hydride samples for the NMR measurements.

It has also been a pleasure to work with L. Lichty, J-W. Han and R. Ibanez-Meier, members in our research group. Finally, I wish to express special appreciation to my wife, Susan H-C. Chang, for her understanding and devotion. She has encouraged me to obtain my goals even though she had to sacrifice many of her personal objectives.

This work was performed at Ames Laboratory under contract No. W-7405-Eng-82 with the U.S. Department of Energy. The United States government has assigned the DOE Report number IS-T 1378 to this thesis.
VIII. APPENDIX
Table A.1  The spark source mass spectrometric analysis for the lanthanum metal La-4783 (Ames Laboratory) which was used in the preparation of the series of LaHx

<table>
<thead>
<tr>
<th>Element</th>
<th>Content (atomic ppm)</th>
</tr>
</thead>
<tbody>
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Rare-earth impurities

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