Proton Motion, Knight Shifts, and Quadrupolar Effects in the Lanthanum-Hydrogen System*

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The nuclear magnetic resonance of both the lanthanum and hydrogen nuclei in the lanthanum-hydrogen system has been studied as a function of hydrogen concentration and temperature. The concentrations ranged from 0.4 H/La to 2.85 H/La and temperatures $-197°C$ to $400°C$. The existence of two phases, part La metal and part $LaH_{2.0}$ for concentrations with less than 2 H/La, is confirmed. Measurements of the proton linewidth and thermal relaxation time T_1 unambiguously demonstrate that proton self-diffusion takes place at moderate temperatures. Activation energies and attempt frequencies for the proton self-diffusion, which are determined as a function of hydrogen concentration, decrease abruptly at ≈ 2 H/La from 23 kcal/mole and 10^{14} sec^{-1}, respectively, to 3 kcal/mole and 10^{11} sec^{-1} at 2.85 H/La. The proton static linewidths vary continuously from 7.8 g at 2 H/La to 12.4 g at 2.85 H/La and the proton T_1 has a characteristic self-diffusion induced minimum of ≈ 5 to 8 msec and a maximum of ≈ 100 msec where spin diffusion to paramagnetic impurities dominates. The self-diffusing protons have a pronounced effect, via a quadrupole interaction, on the La resonances. For hydrogen concentrations slightly greater than 2 H/La, a broadening and then narrowing again of the La linewidth, and a decrease with a subsequent recovery of the La Knight shift is observed as the proton self-duffusion rate increases with temperature. For concentrations greater than 2.4 H/La, no La resonance is observed until a sufficiently high proton self-diffusion rate is attained to average out the quadrupolar effects. A detailed semiquantitative analysis incorporating the proton resonance data is made of these quadrupolar effects. At 400°C the La Knight shift is found to decrease from 0.23% for 2 H/La to 0.10% for 2.85 H/La while no Knight shift is observed for the proton resonance at any concentration or temperature. The thermal relaxation time of the La resonance in $LaH_{2.0}$ is found to be the result of a conduction electron hyperfine interaction with $T_1T = 11.3$ sec $°K$ when the protons are static. With proton motion the La T_1 decreases exponentially to a value somewhat greater than the La T_2 or about 100 μsec at 400°C. A schematic picture of the band structure of the hydride consistent with the available data is suggested, based on an ionized hydrogen atom or proton, whose electron goes into a conduction band localized on the La ion.

I. INTRODUCTION

HYDROGEN will dissolve exothermically in lanthanum metal to form lanthanum hydrides with as many as 3 hydrogen atoms per lanthanum atom. Experimental studies of hydrogen equilibrium vapor pressure versus temperature and hydrogen concentration,[1,2] x-ray diffraction,[3,4] neutron diffraction,[4] and magnetic susceptibility[5] indicate for hydrogen concentrations ranging from less than 2 H per La atom up to almost 2 H per La atom that the hydride is a two-phase system consisting of intermetallic LaH_2 and lanthanum metal. The dihydride LaH_2 has the fcc CaF_2 structure[4] with a lattice constant[3] of $5.661A$ which is larger than the pure metal fcc lattice constant, $5.307A$ at room temperature.

Figure 1 shows the fcc unit cell with lanthanum and hydrogen sites shown.

All of the tetrahedral sites are occupied in the dihydride. As more hydrogen is added, the octahedral sites randomly fill while the tetrahedral sites remain fully occupied. The dihydride exhibits a metallic conductivity 1/100 that of the metal[6] and a paramagnetic susceptibility not much less than the metal. At concentrations near 3 H/La, the hydrides have semiconductor-like electrical conductivity and a diamagnetic susceptibility. A review of other metal hydrides has been prepared by Libowitz.[7]

Previous nuclear magnetic resonance (NMR) investigations of the other metallic hydrides[7-14] have been studies of the proton NMR with one exception,[11] $VH_{0.66}$, in which the vanadium NMR was observed at room temperature. These investigations have demonstrated the usefulness of NMR in studying proton diffusion in the metal hydrides.

It is equally interesting to observe the NMR of the host lattice nucleus for its Knight shift, thermal relaxa-

[1] R. N. R. Mulford and C. E. Holley, J. Phys. Chem. 59, 1222 (1955).
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[4] C. E. Holley, R. N. R. Mulford, F. H. Ellinger, W. C. Koehler, and W. H. Zacherisasen, J. Phys. Chem. 59, 1226 (1955).
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[6] B. Stalinski, Bull. Acad. Polon. Sci. Classe III 5, 1001 (1957).
[7] G. G. Libowitz, J. Nucl. Mat. 2, 1 (1961).
[8] B. Stalinski, C. K. Coogan, and H. S. Gutowsky, J. Chem. Phys. 34, 1191 (1961).
[9] R. E. Norberg, Phys. Rev. 86, 745 (1952).
[10] J. C. Warf, J. Donohue, and K. Hardcastle, Office of Naval Research Tech. Rept. IX, 1959 (unpublished).
[11] R. Oriano, E. McCliment, and J. F. Youngblood, J. Chem. Phys. 27, 330 (1957).
[12] H. C. Torrey, Suppl. Nuovo Cimento 9, 95 (1958).
[13] J. F. Hon, J. Chem. Phys. 36, 739 (1962).
[14] W. Spalthoff, Z. Physik. Chem. Neue Folge 29, 258 (1961).

FIG. 1. Unit cell of LaH₃.

O Lanthanum ions
⊘ Tetrahedral hydrogen ions
● Octahedral hydrogen ions
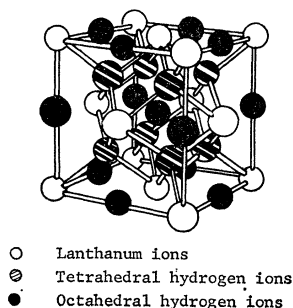
tion time, and linewidths are sensitive to changes in the conduction electron states as well as the presence of stationary or mobile protons. The lanthanum NMR is observable in all of the hydrides of lanthanum in some temperature range. Interesting lanthanum quadrupole interactions, tempered by self-diffusion of the protons, are observed in hydrides of concentrations greater than 2 H/La.

One might expect that, since the electrical conductivity and magnetic susceptibility of LaH_x with $x>2$ decreases with increasing x, the Knight shift of the lanthanum NMR would also decrease. This decrease is indeed observed. (A review of the application of NMR in metals has been published by Rowland.[15])

After a brief summary of experimental apparatus and sample preparation, the results of NMR of protons and lanthanum will be presented separately.

II. EXPERIMENTAL TECHNIQUES

Nearly all measurements of width, shape, and position of the steady-state resonance absorption were taken using a Varian Model V-4210A radio-frequency (rf) unit and crossed coil probes with the signal being fed to a phase-sensitive detector having a bandwidth between $\frac{1}{2}$ and $\frac{1}{5}$ cps and finally displaying the derivative of the resonance absorption line on a graphic recorder. The magnetic field H_0, supplied by a 12-in., $2\frac{1}{8}$-in. gap, electromagnet was modulated at 100 cps and also varied to sweep through the resonances observed at a constant frequency of 7.0 Mc/sec and in some cases 3.5 Mc/sec. The usual practice of designating the linewidth δH or $\delta \nu$ as the separation between the derivative extremum and taking the position or center of the line as the zero of the derivative has been adopted. The sample line shifts were measured relative to an adjacently positioned solution of $LaCl_3$ or water whose resonances were recorded simultaneously.

The T_1 determinations were also made at 7.0 Mc/sec using an NMR pulse apparatus with a crossed coil probe designed and described by Clark.[16] The second free induction decay trace generated by a sequence of two 90° pulses was photographed from an oscilloscope to record the data.

[15] T. J. Rowland, Prog. Mater. Sci. **9**, 1 (1961).
[16] W. G. Clark, Ph.D. thesis, Cornell University, 1961 (unpublished).

Temperatures from -140 to 450°C were obtained by passing cooled or heated nitrogen gas over the sample which was mounted in a platinum "silvered" pipe Dewar designed to fit in the crossed coil probes, while -197°C was obtained by immersing the sample directly in a liquid-nitrogen bath in a finger Dewar.

Hydrides of lanthanum ranging from 0.42 to 2.85 H/La were prepared by a direct union of a known amount of hydrogen gas as determined by its pressure in a closed system of known volume, with a known weight of La metal. La metal which had absorbed 2 H/La or more was quite hard and brittle and easily crushed in a mortar under a dry nitrogen atmosphere as the hydrides appeared to deteriorate in room air, especially if any moisture were present. Small particles between 0.1 and 10 μ in diameter, which was much less than the rf penetration depth, were obtained after crushing in a mortar and then mixed with La_2O_3 to prevent a sintering together when the samples were annealed at 500°C for 12 h or more, and to insulate the particles electrically. A sample was readily degassed by heating to at least 500°C under a vacuum or by mixing in small particles of pure La metal from a completely degassed hydride and heating in a sealed sample tube, to prepare hydrides with less than 2 H/La. All samples were sealed in thin-walled glass tubes approximately 2 cm by 0.8 cm in diameter under their equilibrium vapor pressure of hydrogen with an additional small amount of argon gas to insure good thermal contact with the temperature bath.

The samples reported herein were prepared from La metal obtained from the Michigan Chemical Company, St. Louis, Michigan who gave as major impurities 0.05 to 0.30% paramagnetic rare earths. The only effect observed directly attributable to these impurities was manifested in a T_1 mechanism at low temperatures. The hydrogen used was a chemical electrolytic grade containing perhaps as much as 0.5% oxygen. In some cases this oxygen was removed with a Deoxo unit by freezing out the resultant water, but there were no observable differences between similar samples prepared with or without its use.

III. RESULTS AND DISCUSSION

The results are given separately for the proton and lanthanum NMR with some overlap due to the dependence of some of the lanthanum NMR characteristics upon proton diffusion. For each spin system, measurements of linewidths, thermal relaxation times, and resonance shifts are reported.

A. Proton Magnetic Resonance

A.1 Linewidths, Low Temperature

Magnetic dipole coupling between protons determines the resonance linewidth and the second moment of proton resonance line at low temperatures. Stalinski,
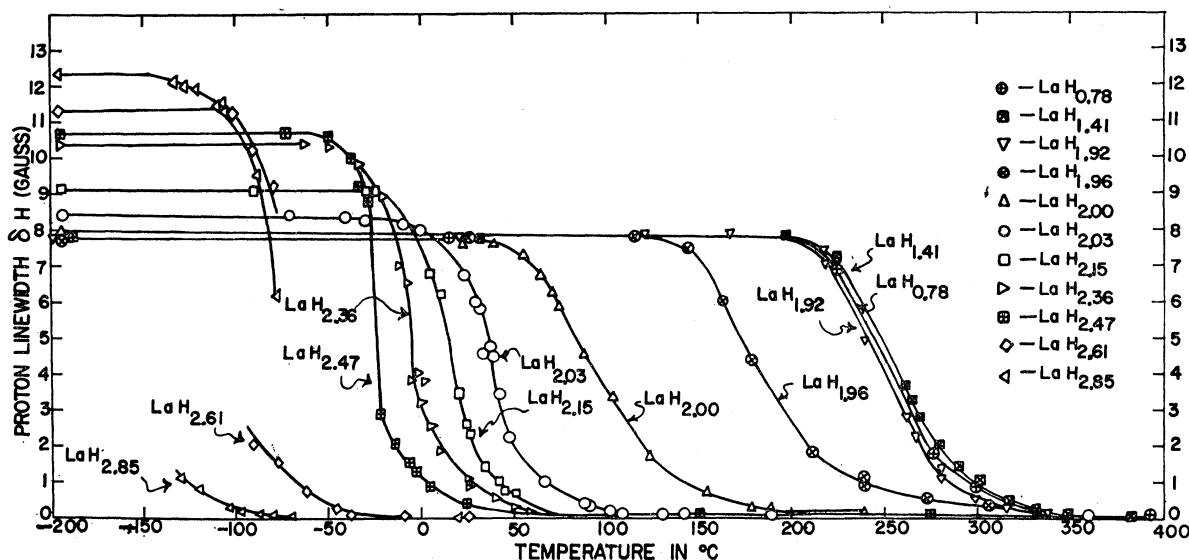
FIG. 2. Temperature dependence of proton linewidths for concentrations ranging from 0.78 H/La to 2.85 H/La.

Coogan, and Gutowsky[8] (SCG), have shown how the second moment of the proton NMR line can distinguish between random population and an ordered arrangement of protons in the tetrahedral or octahedral sites. Since LaH_x with $x<2$ is believed to be a two-phase system of dihydride and lanthanum metal one would expect that the shape of the proton resonance for $x<2$ would be independent of x.

Figure 2 shows the proton NMR linewidth (δH) as a function of temperature for various concentrations of hydrogen. The narrowing of the resonance is apparent at high temperatures. The fact that all samples have a proton linewidth that is constant for some temperature range above $-197°C$ indicates that the protons can be treated as a rigid collection of spins at $-197°C$. Second moments of the proton lines at $-197°C$ will be compared with theory for a rigid lattice.
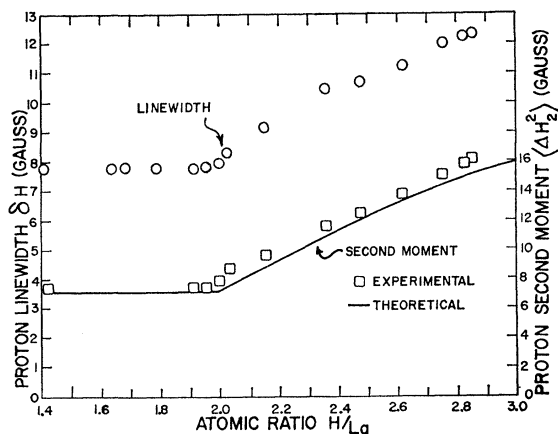

FIG. 3. Concentration dependence of proton linewidth and second moment at a temperature of $-197°C$.

Measurements of the proton NMR second moment were obtained by numerical integration and a plot of these results and linewidths at $-197°C$ are plotted versus hydrogen concentration in Fig. 3. The constant value of second moment and linewidth in LaH_x with $x<1.95$ is consistent with the two-phase nature of the hydride in this concentration range.

The theoretical expression for the proton second moment developed by SCG for random occupancy of tetrahedral and octahedral sites in the fcc lattice is here revised to explicitly include the contribution of the dipole interaction with the nuclear magnetic moments of the host lattice nuclei. Following SCG, the second moment is

$$\Delta H_2{}^2 = f_{oct}(\Delta H_2{}^2)_0 + f_{tet}(\Delta H_2{}^2)_t, \qquad (1)$$

where f_{tet} and f_{oct} are the fractions of protons in each site. Let α and β define the probabilities of occupancy in octahedral and tetrahedral sites, respectively. Then

$$f_{oct} = \frac{\alpha}{2\beta + \alpha} \quad \text{and} \quad f_{tet} = \frac{2\beta}{2\beta + \alpha},$$

and

$$(\Delta H_2{}^2)_0 = c\left(\alpha \sum_p r_{0p}{}^{-6} + \beta \sum_q r_{0q}{}^{-6}\right) + c' \sum_s r_{0s}{}^{-6}, \qquad (2)$$

$$(\Delta H_2{}^2)_t = c\left(\alpha \sum_p r_{tp}{}^{-6} + \beta \sum_q r_{tq}{}^{-6}\right) + c' \sum_s r_{ts}{}^{-6}, \qquad (3)$$

where

$$c = (3/5)I(I+1)\gamma^2\hbar^2,$$
$$c' = (4/15)I'(I'+1)\gamma'^2\hbar^2.$$

The indices p, q, and s designate octahedral, tetrahedral, and host lattice sites, respectively, surrounding

the nucleus at the origin of the summation. From the known values of γ and γ', the gyromagnetic ratios of H and La, and the spins of these nuclei, $I=\frac{1}{2}$, $I'=\frac{7}{2}$, it follows that $c'=0.186c$.

By using lattice sums, evaluated[17] in terms of the fcc lattice constant a_0, and the ratio of c' to c, Eqs. (1), (2), and (3) become

$$\Delta H_2^2(x) = \frac{ca_0^{-6}}{2\beta+\alpha}[115.6\alpha^2+2640\alpha\beta$$
$$+78.4\alpha+1075\beta^2+245.5\beta]. \quad (4)$$

For $x<2$ in LaH_x, the dihydride regions have $\alpha=0$ and $\beta=1$ since the tetrahedral sites are fully occupied. It is useful to define the dihydride second moment ($\alpha=0$, $\beta=1$) as

$$(\Delta H_2^2)_d = 660.5ca_0^{-6} = 7.2 \ G^2. \quad (5)$$

The measured value of second moment is $7.3\pm0.7 \ G^2$ throughout the concentration range with $x<2$ and agrees well with the above theory. If the protons were randomly distributed, the proton second moment would increase with hydrogen concentration as it does in TiH_x.[8] As will be seen in Sec. B.4, the lanthanum NMR data also reflect the two-phase nature of LaH_x with $x<2$.

For concentrations greater than $2H/La$, the measured proton second moment increases monotonically with concentration. It is assumed, in this concentration range, that all tetrahedral sites remain occupied ($\beta=1$) and that octahedral sites fill randomly to become full at $x=3$. This assumption is consistent with observations of quadrupole broadening of the hydride lanthanum NMR discussed in Sec. B of this paper. By taking into account the dependence of a_0 upon concentration,[3] Eq. (4) is, for $x>2$,

$$(\Delta H_2^2(x))_{x\geq2} = \left(\frac{1+0.065\alpha}{2+\alpha}\right)$$
$$\times[0.175\alpha^2+4.12\alpha+2](\Delta H_2^2)_d. \quad (6)$$

Equation (6) is plotted as the solid line in Fig. 3.

The experimental points of Fig. 3 lie consistently above the theoretical curve for $1.95<x<2.85$. Agreement could be improved considerably if tetrahedral sites were assumed to be effectively full at $x=1.95$ with the other 0.05 sites being inaccessible, possibly because of impurities or crystal imperfections. This inaccessibility would also explain the difficulty in hydriding lanthanum completely to $3H/La$. Observations of other investigators[18,19] on the effects of impurities such as O, N, and C on the hydrogen absorption of Zr, Ti,

Pd, and V support the contention that some sites are inaccessible even with very small amounts of impurities. A metallographic study[1] by Mulford and Holley of $LaH_{1.95}$ showed that all the metal had disappeared when this composition was reached. Frenkel defects[20] may be present in concentrations of slightly less than $2H/La$. These defects could have been produced in the high-temperature anneal that each hydride was given.

In the next section of this paper, the characteristics of proton line narrowing are seen to be independent of concentration up to 1.94 H/La and are strongly concentration-dependent at higher proton concentrations. In Sec. B.1 the measurements presented of intensity and linewidth of the hydride lanthanum resonance show changes starting at a minimum concentration of 1.94 H/La which would result if octahedral sites were beginning to fill at this concentration.

A.2 Linewidth, High Temperature

The narrowing of the proton linewidth is due to rapid thermally activated self-diffusion of the protons at high temperatures. The temperature at which narrowing is evident (Fig. 2) is very sensitive to hydrogen concentration for all hydrides with $x>1.94$ and is relatively independent of hydrogen concentrated for $x<1.94$. This concentration independence again reflects the two-phase nature of hydride with $x<1.94$.

Lorentzian-shaped absorption lines are observed in the high-temperature region for all of the samples. Most of the proton resonances narrowed gradually with increasing temperature. Hydrides with $x>2.5$ showed a narrow line superimposed upon a broad line at intermediate temperatures. For these samples only the narrow line was observable at high temperatures. Similar double width character is observed in ZrH_x.[13]

The temperature dependence of the correlation time for proton magnetic dipole interaction is found by fitting the linewidth versus temperature plots to the theory of Kubo and Tomita.[21] This fit is applied in the high-temperature limit where τ_c, the correlation time, is much less than the proton spin-spin relaxation time T'_2. According to Kubo and Tomita,

$$\left(\frac{1}{T_2'}\right)^2 = \left(\frac{2}{\pi}\right)(2\ln2)\langle\Delta\omega^2\rangle \arctan\left(\frac{\pi\tau_c}{4\ln2T_2'}\right), \quad (7)$$

where $\langle\Delta\omega^2\rangle$ is the second moment, in angular frequency units squared, of the rigid lattice resonance line shape. It is assumed that τ_c depends on temperature as

$$(1/\tau_c) = \nu_c = \nu_{0c} \exp(-E_a/RT), \quad (8)$$

where ν_c will be called the "jump frequency" and ν_{0c} the frequency factor. Small uncertainties in E_a produce large uncertainties in ν_{0c} and any more precise definition

[17] H. S. Gutowsky and B. R. McGarvey, J. Chem. Phys. **20**, 1472 (1952).
[18] C. F. Bevington, S. L. Martin, and D. H. Matthews, Proc. Intern. Congr. Pure Appl. Chem. 11th, London, 1947 **1**, 3 (1950).
[19] S. L. Martin and A. L. G. Rees, Trans. Faraday Soc. **50**, 343 (1954).

[20] G. G. Libowitz, Bull. Am. Phys. Soc. **7**, 438 (1962).
[21] R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).

TABLE I. This table is a compilation of the activation energies (E_a) for proton self-diffusion as determined by 4 different experimental methods, and also the values for the attempt frequency (ν_{0c}) from 2 of these methods. The numbers in parenthesis are the nominal temperatures (°C) at which the data for the determinations were taken. The data usually spanned a temperature range of 40°C around the nominal temperature.

| Sample (H/La) | Activation energy (in kcal/mole) ±10% as determined··· | | | | Attempt frequency (in sec^{-1}) ±a factor of 10 as determined··· | |
	from δH_{proton}	from δH_{La}	from $T_{1\,proton}$	from T_{1La}	from $\delta H(=1G)$, proton	from T_1 min., proton
1.41⎫ 1.92⎭	25.3(300)		20(330)	25(190)	2.0×10^{15}	0.74×10^{14}
1.96	10.0(240)				6.6×10^9	
2.00	9.5(150)		6.5(200)		3×10^{10}	1.5×10^{10}
2.03	10.7(70)	10.9(180)			2.8×10^{12}	
2.15	11.2(50)	11.2(180)			2.8×10^{13}	
2.36	9.3(25)	9.8(170)			4.9×10^{12}	
2.47	6.7(0)	9.5(100)	3.0(200),9.5(100),6,2(30)		1.5×10^{11}	3.9×10^{11}
2.61	5.0(−55)	5.3(35)			2.2×10^{11}	
2.85⎫ 2.83⎭	3.7(−110)	2.2(−60)	3.2(130),3.5(−80)		2.3×10^{11}	3.3×10^{10}

and consideration of ν_{0c} than given above is not appropriate for this experiment because of the uncertainties in E_a. At high temperatures Eq. (7) becomes

$$(1/T_2') \approx \langle \Delta\omega^2 \rangle \tau_c \approx (\langle \Delta\omega^2 \rangle / \nu_{0c}) \exp(E_a/RT). \quad (9)$$

Since, for a Lorentzian line, $(1/T_2') = (\sqrt{3}/2)\gamma(\delta H)$, and with $\langle \Delta\omega^2 \rangle = \gamma^2 [\Delta H_2^2(x)]$, Eq. (9) can be more conveniently expressed as

$$\delta H = (2/\sqrt{3})\gamma(\Delta H_2^2(x))(\nu_{0c}^{-1}) \exp(E_a/RT). \quad (10)$$

Equation (10) is fitted to the observed (δH) for each concentration (x) of hydrogen and values of E_a and ν_{0c} determined are listed in Table I. High values of the frequency factors and high activation energies for $x < 1.94$, the dihydride regions, imply that the tetrahedral sites are in a relatively deep, steep-sided potential well. Since all adjacent octahedral sites can hold a hydrogen, there must be a potential maximum between octahedral and tetrahedral sites. The existence of such a maximum would produce deeper, steeper sided tetrahedral site wells than those observed in[22] TiH$_2$ where the octahedral sites are not proton trapping centers.

There is a sharp discontinuity in measured values of E_a and ν_{0c} at $x \approx 1.93$–1.95, the apparent maximum values of x for the dihydride. Values of E_a and ν_{0c} for concentrations $x > 1.95$ are considerably less than those for $x < 1.95$.

At H concentrations of $x < 1.95$, in the dihydride phase, protons diffuse by production of Frenkel defects using the octahedral sites as temporary interstitial positions. The addition of one occupied octahedral site ($x > 1.95$) would, by Coulomb repulsion, lower the activation energies of each of its eight nearest proton neighbors. This lowering then conceivably makes the protons in the adjacent tetrahedral sites more likely

to be excited into one of the next unoccupied octahedral sites (Fig. 1). The resulting tetrahedral site vacancy could then be filled by the original octahedral site proton. By the above outlined steps, the locations of occupied octahedral sites diffuse through the lattice as a point defect. Such a model for diffusion would, because of the Coulomb repulsion near the defect, have a lower activation energy, and a reduced frequency factor than in the dihydride phase. The assumption of randomly distributed octahedral site occupation for $x > 1.95$ is also used in analyzing lanthanum NMR linewidth data in Sec. B. An estimate,[23] of activation energies based upon a point-charge model, where charges are screened by the conduction electrons assuming positive hydrogen ions, and similar to the calculations of Googan and Gutowsky[22] indicates that there should be a sharp decrease in the activation energies at $x = 2.0$ as octahedral sites start becoming occupied. Details of this calculation are in Ref. 23. Diffusion of protons is activated at relatively low temperatures in samples of high hydrogen concentration, where activation energies are found to be less than 5 kcal per mole.

A.3 Thermal Relaxation Time T_1

The time required for the proton spin system to come into thermal equilibrium with its environment, the thermal relaxation time T_1 is affected by self diffusion of the protons. Plots of T_1 versus T or, as in Fig. 4, T_1 versus $(1/T)$ show at high temperatures the characteristic minimum of T_1 that is typical of thermally activated motion.[12] The dipolar interaction between protons and between protons and lanthanum spins is modulated by the thermal motion, and it is responsible for the minimum in T_1. Theory for this model is well

[22] C. K. Coogan and H. S. Gutowsky, J. Chem. Phys. 36, 110 (1962).

[23] D. S. Schreiber, Ph.D. thesis, Cornell University, 1962 (unpublished).

developed[24] and shows that the slope of the $(\ln T_1)$ versus $(1/T)$ plot should be (E_a/R) and $(-E_a/R)$ on the low- and high-temperature sides, respectively, of the minimum. Although the proton relaxation is due to self-diffusing protons, in the presence of unlike La spins the proton system will approach its thermal equilibrium polarization with the usual exponential dependence with just one characteristic relaxation time, T_1. Any tendency for the proton-lanthanum dipolar interaction to change the lanthanum spin polarization will be offset by the fast La thermal relaxation mechanism provided by its quadrupole coupling with the diffusing protons. Approximately constant slopes of the $\ln T_1$ versus $1/T$ plots near the T_1 minimum are found. The values of E_a obtained from these slopes are listed in Table I.

At the temperature of the T_1 minimum, the correlation time is approximately equal to (ω_0^{-1}) where ω_0 is the proton Larmor angular frequency, the relation between τ_c and ω_0 being $\omega_0\tau_c = 1.4$. Use of E_a, τ_c, and T at each T_1 minimum in Eq. (8) results in the values of the frequency factors listed in Table I. For a given sample, the values of the activation energy determined from T_1 data are found to differ from those obtained from line narrowing data. This disagreement either indicates a temperature-dependent E_a, since the determination form T_1 data are for data taken at higher temperatures than the data for line narrowing, or else the simple model used has limited applicability.
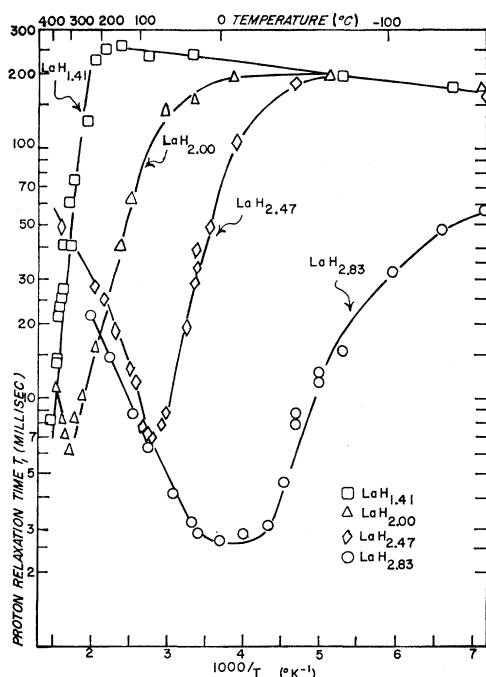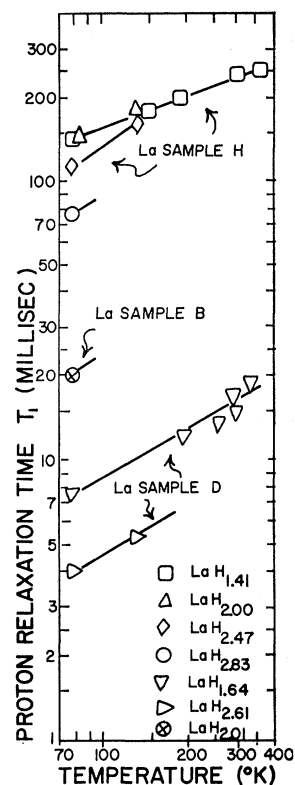

FIG. 5. Proton thermal relaxation times at low temperatures. Lanthanum sample "H" has a major paramagnetic impurity of 500 to 1000 ppm of Er. Sample "D" has 1500 ppm P_r and 3000 ppm Ce. The impurity concentration of sample B is not known.

At low temperatures the value of T_1 levels off with weak temperature dependence. Hydride samples prepared from different lots of lanthanum metal were found to have widely differing values of proton T_1 at 77°K. Low-temperature T_1 values for several samples are shown in Fig. 5. Proton motion is frozen at these low temperatures and the most likely candidate responsible for the thermal relaxation is the mechanism of *spin diffusion*. In contrast to self-diffusion, a spin state can diffuse through the lattice by spin-spin interaction even though the hydrogen ions remain fixed. In regions of the lattice near paramagnetic impurities where the protons are well relaxed the diffusing spin state can also "relax."

Different cases of spin diffusion have been discussed by Blumberg[25] and the only one consistent with the observed data is the spin diffusion limited case where the T_1 is limited in part by the effectiveness of the spin-spin interaction.

For this case,[24]

$$T_1^{-1} = 8.5NC^{1/4}D^{3/4}, \qquad (11)$$

where N is concentration of paramagnetic impurities per unit volume and

$$C = (1/5\pi)(\gamma_p\gamma\hbar)^2 S(S+1)\tau_p(1+\tau_p^2\omega_0^2)^{-1} \qquad (12)$$

with γ_p, S, and τ_p as the impurity gyromagnetic ratio,

FIG. 4. Temperature dependence of proton thermal relaxation time T_1.

[24] A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961).

[25] W. E. Blumberg, Phys. Rev. 119, 79 (1960).

spin, and correlation time of the z component of the impurity spin. D is the spin diffusion coefficient first determined by Bloembergen to be Wa^2 where W is the spin-spin flip rate and a is the diffusion step length.

Samples known to be high in paramagnetic impurities have low values of T_1, where the purest sample used has the longest T_1 at low temperatures. The weak temperature dependence of T_1 most probably results from the temperature dependence of τ_p. In the temperature-range studies it can be safely assumed that $(\tau_p\omega_0)\ll 1$ and that τ_p decreases as T increases. It is then expected that $(1/T_1)\propto\tau_p^{1/4}$. To meet the requirement that $\tau_p\omega_0\ll 1$, it is necessary that $\tau_p\ll 2\times 10^{-8}$ sec in this experiment. An electron spin resonance absorption with a linewidth of 250 G, $\tau_p=5\times 10^{-10}$ sec, was observed.[26] This value of τ_p is compatible with the assumptions above. The fact that the higher the hydrogen concentration, the shorter the value of T_1, as applied to hydrides in a particular subgroup prepared from the same La metal parent sample, say, sample H, and thus having identical paramagnetic impurity content, follows from the dependence of $1/T_1$ on the spin diffusion coefficient D in Eq. (11). The coefficient D dependes upon hydride concentration through its dependence on Wa^2 which increases as the proton concentration increases. The dependence $T_1\propto T^{1/2}$ observed experimentally implies $\tau_p\propto T^{-2}$, which is reasonable.

A.4 Proton Resonance Shift

The expression for the Knight shift which is the result of the contact hyperfine interaction of the s type conduction electrons at the nucleus is given by Knight,[27] as

$$\left(\frac{\Delta H}{H}\right)=\left(\frac{K_H}{100}\right)=\frac{a(s)I}{2\mu_I\mu_\beta}\chi_p M\xi,$$

where $a(s)$ is the hyperfine coupling constant, μ_I is the nuclear magnetic moment, and μ_β the Bohr magneton. $(\chi_p M)$ is the average susceptibility per atom when χ_p is in terms of cgs/g and M is the atomic mass, $M=M_{La}+2M_H$ for $LaH_{2.0}$, and $\xi=p_F/p_A$ where p_F is the probability density at the nucleus averaged over the conduction electrons near the Fermi surface and p_A is the probability density at the nucleus for the free atom. For hydrogen $a(s)=0.04$ cm^{-1} and χ_p for $LaH_{2.00}$ is taken as[12] $\chi_p=0.42\times 10^{-6}$/g assuming this measured value of the bulk susceptibility to be primarily the spin susceptibility.

Hence, $K_H=0.15\xi_H\%$. Since no Knight shift is observed for the proton within the experimental error of 0.001%, then $0.001>0.15\xi_H$, $\xi_H<6\times 10^{-3}$. This is suggested evidence for the ionization of the hydrogen so that its $1s$ band is nearly empty. ξ will be even less than this for greater H/La ratios since the susceptibility decreases.

Perhaps a better way of expressing K_H is in terms of K_{La} for $LaH_{2.0}$ since then it does not depend on the average susceptibility. The ratio of Knight shifts for H and La is then simply

$$\frac{K_H}{K_{La}}=\frac{a(s)_H I_H\xi_H}{a(s)_{La} I_{La}\xi_{La}}=\frac{0.04\xi_H}{\xi_{La}},$$

where[27] $a(s)_{La}=0.13$ cm^{-1} which gives, putting in the measured value of $K_{La}=0.23\%$, $\xi_H<0.1\xi_{La}$ showing that the conduction electrons favor the La nucleus more than they do the proton.

B. Lanthanum Magnetic Resonance

The resonance, linewidth, relaxation time, and shift of lanthanum NMR in the hydrides are all sensitive to the hydrogen concentration. Presence of hydrogen can change the symmetry of the La environment and produce an electric quadrupole interaction which perturbs the Zeeman levels and leads to a striking temperature-dependent broadening as well as an additional thermal relaxation mechanism. Electronic band structure changes due to hydriding change the LaT_1 as well as the Knight shift of the resonance. From the quadrupole effects on the La linewidth it is concluded that the quadrupole interaction is short ranged and that the use of a Mott screening constant is appropriate. The effect of hydriding on the electronic band structure of the hydride does not follow conclusively from the NMR data but some tentative interpretations are made.

B.1 Linewidth, Intensity, and Shift at Low Temperatures

For any one hydride the low-temperature range is defined as that temperature range where the protons are in fixed lattice sites and self-diffusion is negligible. Figure 6 shows the effects on the La resonance when the composition of hydrogen in LaH_x is increased from what shall be termed "deficient" $(x<2)$ to "dilute" $(2<x<2.3)$.

Nearly all the features can be interpreted by considering the quadrupole interaction which is the result of more and more La nuclei experiencing a noncubic environment of protons and, hence, being perturbed by electric field gradients.

The deficient concentrations show no quadrupole interaction indicating proton-filled tetrahedral sites $(\beta=1)$ and vacant octahedral $(\alpha=0)$ sites. Moreover, the linewidth of the La resonance calculated from the theoretical second moment agreed to within 20% with the experimental value. The strength of the quadrupole interaction arising from field gradients produced by protons in the octahedral sites can be conveniently expressed by the frequency[28] $\nu_Q=[3e^2qQ/2I(2I-1)h]$, where[29] $Q\approx(0.3\pm 0.2)\times 10^{-24}$ cm^2 and $q=(B/r^3)$

[26] E. L. Wolf and S. H. Christensen (private communication).
[27] W. D. Knight, Solid State Phys. 2, 93 (1956).

[28] M. H. Cohen and F. Reif, Solid State Phys. 5, 321 (1957).
[29] K. Murakawa and T. Kamei, Phys. Rev. 105, 671 (1957).

$\times [1+kr+(kr)^2/2] \exp(-kr)$ which has been derived from the screened potential

$$\phi(r) = (1/r) \exp(-kr).$$

B is a factor which takes into account antishielding and polarization effects.[28] For the dilute concentrations to be discussed below, the free electron value of $k = 2 \times 10^8$ cm^{-1} has been used while for the high concentrations $(x > 2.3)$ a value of k decreased from that of the dilute concentrations must be considered to be consistent with the loss of metallic character.

In terms of ν_Q a line broadened by a first-order quadrupole interaction will have a contribution to the line-width $\delta\nu_{Q1}$ which is just the order of ν_Q and which is manifested by a distribution of splittings of the satellite transitions, those with $|m| \leftrightarrow |m-1|$, and $|m| > 1/2$, away from the central line $(m = -1/2) \leftrightarrow (m = 1/2)$. When the interaction is strong enough so that second-order perturbation theory is applicable, the line will only consist of the $(m = -1/2) \leftrightarrow (m = 1/2)$ transitions, the satellites having been so shifted and broadened as to be unobservable, and the width $\delta\nu_{Q2}$ will be the order of the separation of the two components of the central lines, or $(25/9)A$ (sec^{-1}), $A = [I(I+1)-3/4] \times \nu_Q^2/16\nu_0)$ sec^{-1}. In this case there will also be a shift K_Q of the center of gravity of the two component line which is $(-2/3)A/\nu_0 \times 100\%$. When only the $(m = 1/2) \leftrightarrow (m = -1/2)$ transitions contribute to the line, the intensity is reduced to 19% of the full line which would include the satellites.

The effective quadrupolar widths which must be greater than the magnetic dipolar width $\delta\nu_d \approx 3 \times 10^3$ (sec^{-1}) to be considered as observable and shifts at 7 Mc/sec for the 6 nearest neighbor La nuclei at a distance $r = (1/2)a_0$ from an occupied octahedral site are

$$\delta\nu_{Q1}^{(6)} = 1.5 \times 10^3 B \text{(sec}^{-1}),$$
$$\delta\nu_{Q2}^{(6)} = 9 \times 10^{-1} B^2 \text{(sec}^{-1}),$$
$$K_Q^{(6)} = -3 \times 10^{-6} B^2 \text{(sec}^{-1}),$$

while for the 8 next nearest neighbors at $r = a_0/\sqrt{2}$,

$$\delta\nu_{Q1}^{(8)} = 3 \times 10^2 B^2 \text{(sec}^{-1}),$$
$$\delta\nu_{Q2}^{(8)} = 3.5 \times 10^{-2} B^2 \text{(sec}^{-1}),$$
$$K_Q^{(8)} = -1 \times 10^{-6} B^2 \%.$$

Reasonable agreement with the observed results of Fig. 6 can be obtained if B is taken as approximately 50. For the 6 nearest neighbors only the central line is observed with the possibility of a second-order broadening which is further enhanced at 3.5 Mc. The 8 next nearest neighbors are only broadened by the first-order quadrupole interaction. Hence, the observed relative intensity should decrease, since only the central line is observed for the 6 nearest neighbors, as $I/I_0 \approx 0.19(6\alpha) + (1-6\alpha) \approx (1-4.8\alpha)$, $\alpha \leq 0.25$, which gives the slope of I/I_0 versus α as 4.8 to be compared with that ob-
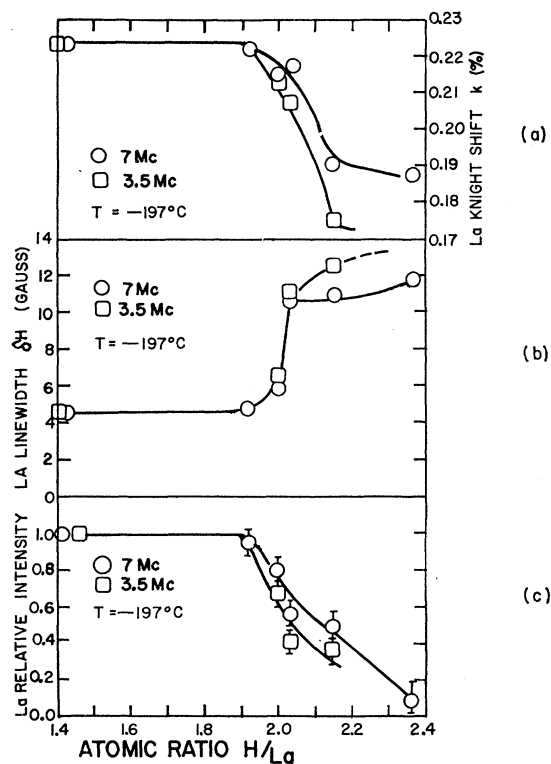

FIG. 6. Intensity, linewidth, and Knight shift of lanthanum nuclear magnetic resonance versus concentration. All data recorded at $-197°$C.

served for the quite dilute concentrations, which is about 4.

It should be noted that a simultaneous reduction in k and B to 0.7×10^8(cm^{-1}) and 5, respectively, would also be consistent with the observed data. While the lower value of k might seem reasonble, the value of B however, is much too small. A typical value for a large Z ion such as La, excluding polarization effects, is about 100. A value of B equal to 70 for Ce^{3+} has been calculated.[30] The fact that no La resonance is observed at 2.85 H/La (at $-197°$C), which has the same effective concentration of proton defects at 2.15 H/La, and that the intensity of the resonance observed when rapid proton self-diffusion has averaged out the proton-induced quadrupole interaction, is only $\frac{1}{4}$ of the expected intensity of all $|\Delta m| = 1$ transitions leads one to suspect that other imperfections or stacking faults of this more weakly bound lattice are the source of electric field gradients, and that they are less shielded as a result of a decreased screening constant k.

B.2 Linewidth, High Temperature

At high temperatures where the self-diffusion of protons is considerable the lanthanum linewidth of

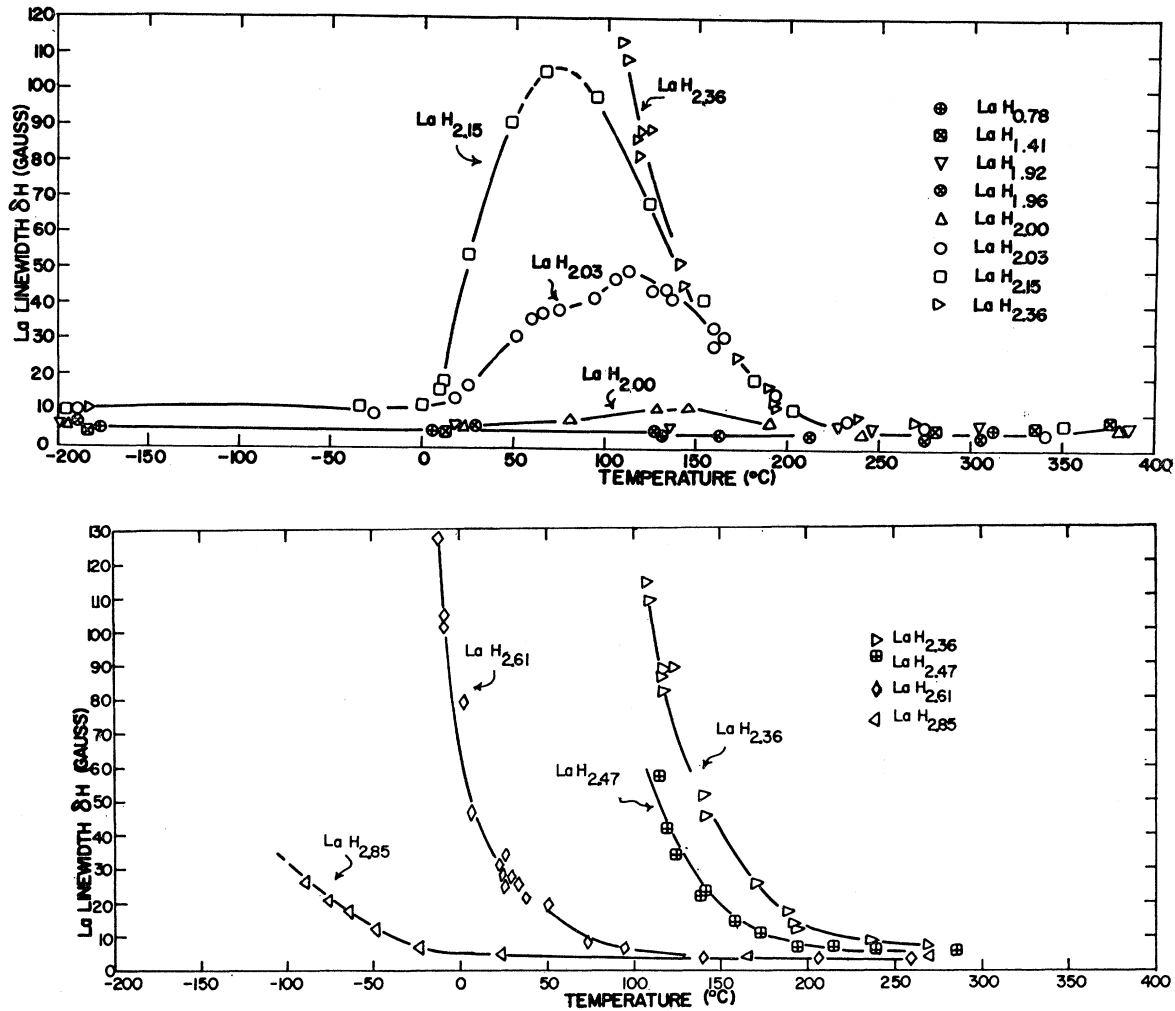[30] R. E. Watson and A. J. Freeman, Bull. Am. Phys. Soc. 8, 24 (1963).

Fig. 7. Temperature dependence of lanthanum NMR linewidth for concentrations ranging from 0.78 H/La to 2.85 H/La.

dilute $(2<x<2.3)$ samples first broadens and then narrows as the temperature is increased. These effects are shown in Fig. 7. A decrease in the Knight shift accompanies the peak in the broadening which is itself field-dependent and all indications are that a quadrupole interaction with diffusing protons is responsible for linewidth changes. The most convenient way to understand these effects is by thinking in terms of the characteristic La spin dephasing time, or transverse relaxation time T_2. The relation between the linewidth and T_2 is $\delta\nu \approx (1/\pi T_2)$.

Some times which are characteristic of the diffusion process will first be defined and then related to their effect on T_2. In the above discussion of low-temperature linewidths it was pointed out that the quadrupole interaction is short ranged in the dilute hydrides. It can then be assumed that an occupied octahedral site in the LaH$_2$ lattice, which will be treated as a point defect, will perturb only those La nuclei within a critical radius r_0

of the point defect by a characteristic frequency $\nu_{Q0} = (\omega_{Q0}/2\pi)$. The assumption that only the octahedral site protons are responsible for the quadrupole interaction is reasonable since no diffusion-dependent La line broadening is observed in the deficient concentrations for which $\alpha = 0$.

As the defects begin to diffuse, the particular region within r_0 is only perturbed for a time τ_r and the condition that these nuclei be dephased by the quadrupole interaction is $\omega_{Q0}\tau_r \gtrsim 1$ rad. The quantity $\omega_{Q0}\tau_r$ is the difference in phase between a La nuclear spin exposed to the additional quadrupole interaction compared to one that does not experience the quadrupole interaction. The exposed spin is considered to be effectively dephased and no longer contributing to the resonance signal when $\omega_{Q0}\tau_r > 1$. τ_r can be expressed in terms of the proton jump time τ_c by considering the random-walk problem. As the temperature increases, τ_r decreases. A defect which jumps a distance a (an

adjacent octahedral-tetrahedral separation) will, after n jumps, move a mean distance r_0, where $n = (r_0/a)^2$. Hence, it spends a mean time $\tau_r = n\tau_c = (r_0/a)^2 \tau_c$ within r_0 of a particular La nucleus. Thus, if every La nucleus is "visited" (the effect comes within r_0) by the defect on the average once every τ_v sec, the nucleus will be dephased every τ_v seconds so that (and providing $\omega_{Q0}\tau_r > 1$)

$$1/T_2 = 1/T_{2d} + 1/\tau_v, \qquad (13)$$

where T_{2d} is the ordinary magnetic dipolar dephasing time, can be best obtained from the "visit" rate.

For simplicity, consider that the distribution of defects in the "dilute" concentration with $x = 2 + \alpha$ and a density $\rho = (4\alpha/a_0^3)$ is homogenous throughout the lattice. Any one La nucleus is selected, and the rate at which defects diffuse to within r_0 of it will be estimated. The number to defects dN in a spherical shell of thickness dR and a radius R about the La nucleus will diffuse a mean distance R in a mean time $\tau = (R/a)^2 \tau_c$ where τ_c and a are the elementary jump time and distance, respectively. The effective number of defects which diffuse to within r_0 of the La nucleus after moving R is just $(\pi r_0^2/4\pi R^2)dN$. Hence, the rate at which defects from the shell dR arrive within r_0 of the La nucleus is just

$$\frac{(\pi r_0^2/4\pi R^2)dN}{(R/a)^2 \tau_c}.$$

The net rate for all such spherical shells is then (since $dN = \rho 4\pi R^2 dR$)

$$\frac{a^2 \pi r_0^2 \rho}{\tau_c} \int_{r_0}^{\infty} \frac{dR}{R^2} = \frac{a^2 \pi r_0 \rho}{\tau_c}. \qquad (14)$$

The mean time τ_v between arrival of the defects is just the reciprocal of the rate or

$$\tau_v = \frac{\tau_c}{a^2 \pi r_0 \rho} = \left(\frac{4a_0}{3\pi r_0 \alpha}\right)\tau_c, \qquad (15)$$

with $a = (\sqrt{3}/4)a_0$ the octahedral-tetrahedral separation.

With a low concentration of defects, and at low temperatures $(\omega_{Q0}\tau_r > 1)$,

$$\frac{1}{T_2} = \frac{1}{T_{2d}} + \left(\frac{3\pi r_0 \alpha}{4a_0}\right)\frac{1}{\tau_c}, \qquad (16)$$

since τ_c depends on temperature as $\tau_c = (\nu_{0c})^{-1} \times \exp(Ea/RT)$, then as temperature increases, the linewidth increases so long as the restriction $\omega_{Q0}\tau_r > 1$ is valid.

At very high temperatures, when $\omega_{Q0}\tau_r < 1$, the amount of dephasing produced by each visit every τ_v seconds will not be sufficient to dephase the La nuclei. Since the dephasing per visit is small and random in sign, then the phase difference will accumulate random-
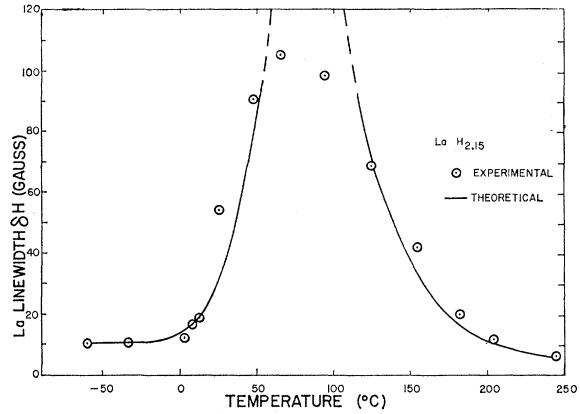

FIG. 8. Linewidth of lanthanum NMR in LaH$_{2.15}$ versus temperature with theoretical fit obtained by adjusting ω_{Q0}.

walk fashion and after n visits the average accumulated phase is $n^{1/2}(\omega_{Q0}\tau_r)$. When $n^{1/2}\omega_{Q0}\tau_r$ equals 1 rad the spins are considered to be dephased, and the time required for n visits and a phase accumulation of one radian is $n\tau_v = \tau_v/(\omega_{Q0}\tau_r)^2$.

Therefore, at high temperatures

$$\frac{1}{T_2} = \frac{1}{T_{2d}} + \frac{(\omega_{Q0}\tau_r)^2}{\tau_v}, \qquad (17)$$

$$\frac{1}{T_2} = \frac{1}{T_{2d}} + \frac{64\pi r_0^5 \alpha \omega_{Q0}^2 \tau_c}{3a_0^5}. \qquad (18)$$

Equation (18) follows from Eq. (17), Eq. (14), and the value of the step length, $a = (\sqrt{3}/4)a_0$. It follows from Eq. (18) that the linewidth should narrow at high temperatures through the dependence of τ_c on temperature,
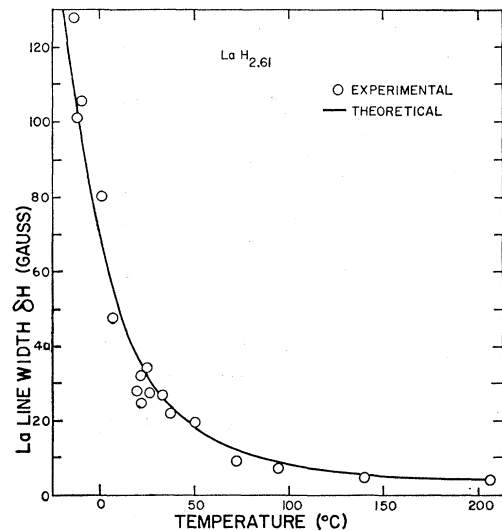

FIG. 9. Linewidth of lanthanum NMR in LaH$_{2.61}$ versus temperature with theoretical fit obtained by adjusting ω_{Q0}.
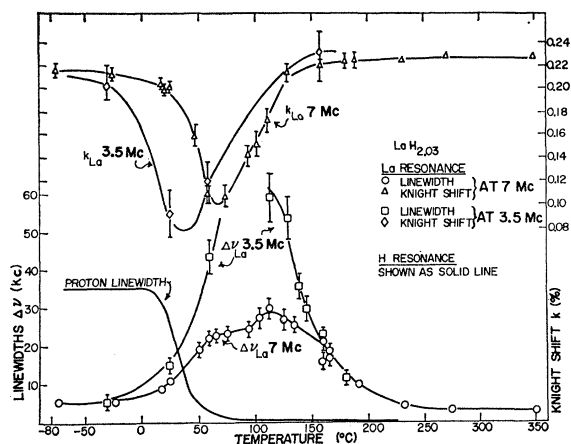
Fig. 10. Temperature dependence of lanthanum linewidth and Knight shift in $LaH_{2.03}$.

Eq. (8). Measurements of E_a obtained from a linewidth data in this temperature region are given in Table I.

A reasonable value of r_0 is $(1/2)a_0$, the octahedral proton-La nearest neighbor distance, and $\omega_{Q0} \approx 1 Mc/sec$, which is close to that obtained in the previous section, are substituted into Eq. (16) and plotted in the low-temperature region in Fig. 8 for $LaH_{2.15}$ using the relation $\delta H \approx (2/\gamma T_2)$. For the high-temperature narrowing given by Eq. (17) and plotted in Fig. 8 it is found that the best fit to the experimental data implies a value for $\omega_{Q0} \approx 3$ Mc/sec. A similar plot is made for $LaH_{2.61}$ in Fig. 9 taking $\omega_{Q0} \approx 2$ Mc/sec. Similar agreement is obtained using Eq. (16) and (18) for $LaH_{2.03}$, $LaH_{2.36}$, $LaH_{2.47}$, and $LaH_{2.85}$ for which no theoretical curves are shown, but a tabulation of values of ω_{Q0} for which the agreement was obtained is given in Table II. For the dilute concentrations, α and r_0 can be taken as previously defined, but for high concentration the proper values are somewhat uncertain. The quantity α no longer represents the number of defects for the high concentrations ($x \geq 2.5$) since the new "defect-free" LaH_3 structure is obtained when $\alpha = 1$. Rather than α, $(1-\alpha)$ is used to replace it.

The effective values of the quadrupole coupling constant ω_{Q0} are seen to vary between 1 and 3 Mc/sec. This variance most likely arises from the oversimplification of the theory in that one value of r_0 and one value

TABLE II. La quadrupole coupling constants obtained from La linewidth narrowing data.

Sample (H/La)	$\omega_{Q0}(sec^{-1}) \pm (0.5 \times 10^6)$
2.03	3×10^6
2.15	3×10^6
2.36	3×10^6
2.47	2×10^6
2.61	2×10^6
2.85	1×10^6

of ω_{Q0} are chosen to represent what in reality must be a distribution of these quantities.

The temperature-dependent quadrupolar contribution to the La linewidth depends on α in both the low- and high-temperature limits, Eq. (16) and Eq. (18), and this dependence on α is evident in Fig. 7.

The actual line shapes for $LaH_{2.03}$ in the broadening and then narrowing temperature regions of the La linewidth are shown in Fig. 10 followed by the extracted data of the Knight shift and linewidth in Fig. 11. The decreased shift, the magnitude of the decrease being K_Q, the frequency dependence of the width, and the absence of pronounced wings clearly show the quadrupole interaction to be strong enough so that only second-order effects are prominent, while at the high temperature with the linewidth narrowing again, the restoration of the shift to its previous value, the frequency independence of the width, and the appearance of long wings showing the contribution to the line of the satellite transitions indicate that the quadrupole interaction is weakened to the extent that only first-order quadrupole effects are observed. It is worthwhile to note that the approximate relation between K_Q and the linewidth
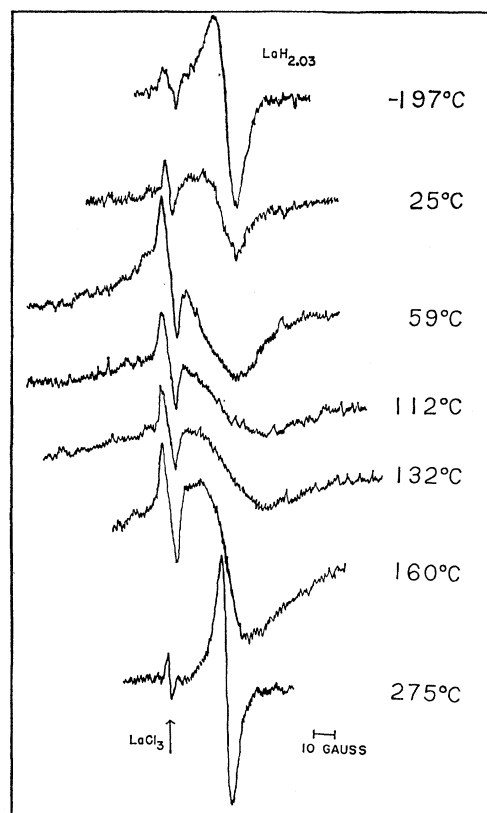

Fig. 11. Recorded derivative of lanthanum NMR absorption versus magnetic field in $LaH_{2.03}$ at various temperatures. These show the effect of the proton diffusion on the linewidth and shift relative to the $LaCl_3$ reference sample which is kept at room temperature.

$\delta\nu_{Q2}$ given by $K_Q = -0.24(\delta\nu_{Q2}/\nu_0)\%$ is approximately obeyed on the low-temperature side of the line-broadening region.

B.3 Thermal Relaxation

Two distinct thermal relaxation mechanisms in LaH$_{1.41}$ are apparent from Fig. 12, one having a $T_1 \propto (1/T)$ at low temperatures and $\ln T_1 \propto (1/T)$ at high temperatures. The sharp drop in T_1 at the very beginning of proton self-diffusion indicates a strong proton diffusion-dependent relaxation mechanism, which can be effected through either the magnetic dipole or electric quadrupole interaction. The magnetic dipolar interaction is found to be negligible compared to that of the quadrupole interaction. The fluctuating electric field gradients of the diffusing protons can induce transitions which provide the relaxation. The quadrupolar Hamiltonian has nonvanishing matrix elements for the transitions $|m\pm1| \leftrightarrow |m|$, $|m\pm2| \leftrightarrow |m|$, if there is a finite intensity at ν_0 and $2\nu_0$ in the Fourier spectrum of the time varying field gradients. The transition probabilities for all such transitions can be determined, and when summed in the appropriate way, give T_1.

The matrix elements of interest tabulated below are taken from Cohen and Reif.[28]

$$\langle m\pm1|H_Q|m\rangle = A(2m\pm1)[(I\mp m)(I\pm m+1)]^{1/2}V_{\mp1},$$

$$\langle m\pm2|H_Q|m\rangle = A[(I\mp m)(I\mp m-1)(I\pm m+1)$$
$$\times (I\pm m+2)]^{1/2}V_{\mp2},$$

where

$$A = eQ/4I(2(-1)), \quad V_{\pm1} = V_{xz}\pm iV_{yz},$$
$$V_{\pm2} = 1/2(V_{xx} - V_{yy})\pm iV_{xy}$$

$(V_{ij} = \partial^2 V/\partial x_i \partial x_j)$, where V is the potential. The transition probabilities can be expressed in terms of Fourier intensities $J(\omega)$.[24]

$$J(\omega) = \langle F(t)F^*(t)\rangle_{av} 2\tau_c(1+\omega^2\tau_c^2)^{-1},$$

where τ_c is the correlation time or $(1/\tau_c) = \nu_c$ the proton jump frequency and the F's are the position functions appearing in the V's for the interaction considered here. If the potential V is of the form employed previously,

$$V = eB(e^{-kr})/r, \quad k \approx 2\times10^8 \text{ cm}^{-1},$$

then

$$V_{\pm1} = \frac{3B(e^{-kr})}{r^3}(1+kr+\tfrac{1}{2}(kr)^2)\cos\theta\sin\theta e^{\pm i\phi}$$

and

$$V_{\pm2} = \tfrac{3}{2}B\frac{e^{-kr}}{r^3}(1+kr+\tfrac{1}{2}(kr)^2)\sin^2\theta e^{\pm2i\phi},$$

so that the F's are given by

$$V_{\pm1} = 3BF_1[r(t),\theta(t),\phi(t)],$$
$$V_{\pm2} = \tfrac{3}{2}BF_2[r(t),\theta(t),\phi(t)].$$
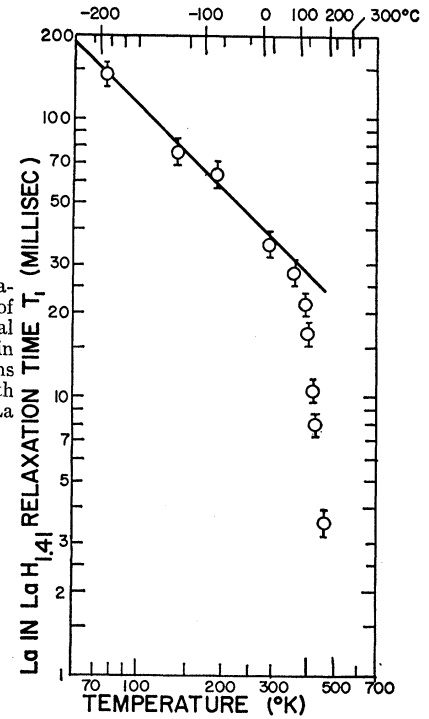

FIG. 12. Temperature dependence of lanthanum thermal relaxation time in the dihydride regions of a sample with average 1.41 H/La concentration.

Hence, the transition probabilities $W_{(m\pm1, m)}$ and $W_{(m\pm2, m)}$ expressed in terms of the J's are just

$$W_{(m\pm1, m)} = (1/\hbar^2)(3BA)^2(2m\pm1)^2$$
$$\times[(I\mp m)(I\pm m+1)]J_1(\omega_0),$$

$$W_{m(\pm2, m)} = (1/\hbar^2)(\tfrac{3}{2}BA)^2(I+m)(I\mp m-1)$$
$$\times (I\pm m+1)(I\pm m+2)J_2(2\omega_0).$$

The appropriate way to sum the W's to obtain T_1,

$$1/T_1 = \tfrac{1}{2}\sum_{m,n}(E_n-E_m)^2 W_{m,n}/\sum_n E_m^2,$$

where

$$E_m = mh\nu_0, \quad \sum_m E_m = 0,$$

was shown by Hebel and Slichter[31] to be valid for a spin system with equally spaced energy levels and describable by a spin temperature.

For any value of I, the result is

$$\frac{1}{T_1} = \frac{9(Be^2Q)^2(2I+3)}{40\hbar^2I^2(2I-1)}[J_1(\omega_0)+J_2(2\omega_0)],$$

and for $I = \tfrac{7}{2}$,

$$\frac{1}{T_1} = \frac{3(Be^2Q)^2}{\hbar}[J_1(\omega_0)+J_2(2\omega_0)].$$

The procedure for evaluating the J's is identical to that carried out in calculating the proton relaxation

[31] L. C. Hebel and C. P. Slichter, Phys. Rev. 113, 1504 (1959).

time. To include the effect of all the protons the J's are multiplied by the total number of protons. Hence, for example,

$$J_1(\omega_0) = \frac{n}{a_0^3} \int_a^\infty dr \int_0^\pi d\theta \int_0^{2\pi} d\phi |F_1|^2 r^2$$
$$\times \sin\theta 2\tau_c/(1+\omega_0^2\tau_c^2),$$
$$J_1(\omega_0) \approx \frac{128\pi}{15a_0^3} \int_a^\infty dr[(e^{-kr}/r)(1+kr+(kr)^2/2)]^2$$
$$\times 2\tau_c/(1+\omega_0^2\tau_c^2),$$

where n is the number of protons per unit cell. For the only sample considered here, $LaH_{1.41}$, $n=8$ and $a = a_0\sqrt{3}/4$ is the distance of closest approach of a charged proton to a La nucleus in the diffusion process.

The r integral is evaluated with the result that, for $\tau_c\omega_0 \gg 1$, the region of interest

$$1/T_1 \approx B^2/3 \times 10^5 \tau_c, \quad \tau_c = (\nu_{0c})^{-1} \exp(E_a/RT), \quad (19)$$

an activation energy of 25 kcal/mole is obtained from the slope of the straight line of T_1 versus $1/T$ on a semi-log plot which is in substantial agreement with that obtained by other methods and compiled in Table I. As a further check on Eq. (19), ν_{0c} can be calculated from a measured T_1 for a particular temperature and compared with that obtained from the proton line-narrowing data with the result that with $B \approx 50$,

$$\nu_{0c} = 6 \times 10^{15} \text{ sec}^{-1},$$

which is an unusually large value of ν_{0c} but not out of line with the other determinations. An uncertainty in E_a of 10% can produce an order of magnitude variation in the determination of ν_{0c}.

That the product T_1T is observed (Fig. 12) to be a constant equal to 11.3 sec °K at low temperatures where proton motion and, hence, any time-varying quadrupole interaction relaxation mechanism is frozen out, is a consequence of the contact hyperfine interaction of the conduction electrons which also produces the Knight shift. The explicit expression for the temperature dependence of T_1 in metals given by Korringa[32], and in a slightly modified form by Pines[33] is shown here, $1/T_1 = (\pi kT/4\hbar)\Omega^2 g^2(E_f)\xi^2 a^2(s)$, where Ω is the atomic volume, $g(E_f)$ is the density of states at the Fermi surface, ξ is the ratio of the probability density at the nucleus averaged over the conduction electrons at the Fermi surface to the probability density at the nucleus for the free atom, and $a(s)$ is the hyperfine coupling constant. Alternatively, the Korringa relation, $T_1T(\Delta H/H)^2 = (\hbar/4\pi k)(\gamma_e/\gamma_n)^2$, without taking into account electron-electron correlations, can be used to calculate the Knight shift for comparison to the observed value of $K=0.23\%$ to be discussed in the next section. The measured value of K is larger by a factor of 2.1 than that predicted by the Korringa relation and

[32] J. Korringa, Physica 16, 601 (1950).
[33] D. Pines, Solid State Phys. 1, 367 (1955).

the measured value of T_1. This enhancement of the shift could be due to electron correlation effects or a contribution of an orbital susceptibility as discussed by Clogston et al.[34] and Orgel.[35] The fact that non-s type conduction electrons do not contribute to the relaxation but can make a sizable contribution to the observed Knight shift through their non-negligible orbital susceptibility makes the latter explanation quite plausible. It should be noted that the enhancement of the Knight shift in pure La metal is only 1.15 times which suggests that there is relatively twice as much non-s character, and most likely it is d character, in the conduction band of the hydride over that of the pure metal.[36]

B.4 Knight Shifts

The La Knight shift, as might be expected, is strongly dependent on the hydrogen concentration and somewhat on temperature aside from the negative contribution due to the second-order quadrupole interaction appearing at the onset of proton self-diffusion as discussed previously. It should be noted that the hydride La Knight shift is independent of concentration for LaH_x where $0 < x \lesssim 2$ in such samples two La resonances are observable: one from the material hydrided to $x=2$ and the other from the remaining La metal. The separated two-phase nature of the hydride is again evident.

In LaH_x, several interactions could be responsible for the Knight shift. Since La has partially full d and s bands, the s electron spin susceptibility, the d-electron spin susceptibility through an s electron-d conduction electron exchange, and the d orbital susceptibility can all contribute to K. The contribution to K can be expressed as $K = C_1\chi_s + C_2\chi_d + C_3\chi_{orb}$, where χ_s is the s-conduction electron paramagnetic susceptibility, χ_d is the d-conduction electron paramagnetic susceptibility, and χ_{orb} is the contribution through second-order orbital paramagnetism.

The variation of K with H concentration shown in Fig. 13 at 400°C, where the static quadrupole interactions have been averaged out by rapid proton self-diffusion, is qualitatively consistent with the dependence of susceptibility upon H concentration. Measurements of χ for La metal and the hydrides indicate that the measured susceptibility has weak temperature dependence in the metal and no temperature dependence in LaH_2. As mentioned earlier, LaH_x becomes diamagnetic for $x \approx 2.65$. When the H concentration approaches 3H/La, the electrical conductivity measured

[34] A. M. Clogston, A. C. Gossard, V. Jaccarino, and T. Yafet, Phys. Rev. Letters 9, 262 (1962).
[35] I. Orgel, J. Phys. Chem. Solids 21, 123 (1961).
[36] Note added in proof. With respect to Sec. B.3, a contribution to T_1 from orbital momentum of conduction electrons may be significant in the La-H system. Recent work by J. Butterworth on the V-Cr system and theoretical considerations of Y. Obata indicate the possibility of such a T_1 mechanism. We would like to thank J. Butterworth for informing us of these studies prior to their publication.

by Stalinski changes from metallic type conductivity to semiconductor character, and the La resonance shift approaches zero. The change in χ and metallic character of the hydrides with hydrogen concentration suggests that the Knight shift should be strongly concentration-dependent.

The temperature dependence of the Knight shifts are shown in Fig. 14. The concentrations with more than 2H/La show no appreciable temperature dependence aside from the negative second-order quadrupolar shift previously mentioned. The deficient concentrations, with less than 2H/La, show a gradual increase in shift from $-197°C$ up to the temperature at which proton self-diffusion begins. The volume expansion effect or the so called $V^{2/3}$ effect is too small by a factor of 10 to account for this increase; however, a change in the susceptibility, too small to be discernable in Stalinski's plot of χ versus T which shows χ independent of T, could account for this behavior. A weak-temperature dependence in χ could come from an electron-phonon interaction or a temperature-dependent χ_d. It is worthwhile to point out that the susceptibility of pure La metal is observed to increase from $0.75\times10^{-6}/\text{g}$ at $300°K$ to $1.5\times10^{-6}/\text{g}$ at $4.2°K$. Paralleling this is an increase in the pure metal Knight shift at $4.2°K$ by 15% over its room-temperature value. On the other hand the La Knight shift in $\text{LaH}_{2.0}$ at $4.2°K$ was essentially unchanged from its value at $-197°C$ so at least K_{La} and χ are consistent, if Stalinski's susceptibility measurements are extrapolated as being temperature-independent to $4.2°K$.

The rather large increase in the Knight shift in the deficient concentrations, especially in the 1.41 and 0.78 H/La samples, with increasing temperature above the point at which proton self-diffusion has set in, is quite possibly the result of hydrogen diffusing from the $\text{LaH}_{2.0}$ portion of the sample into the La metal portion, thereby creating an averaged deficient composition
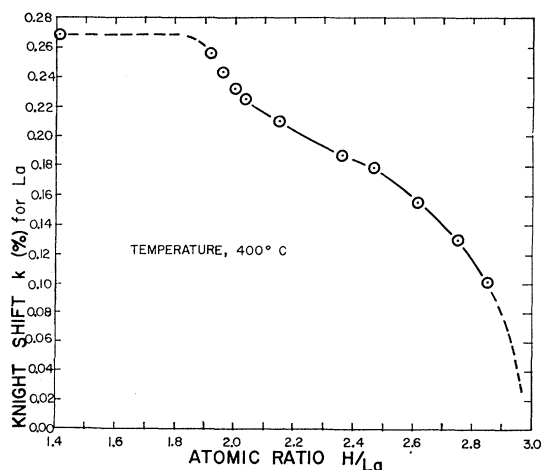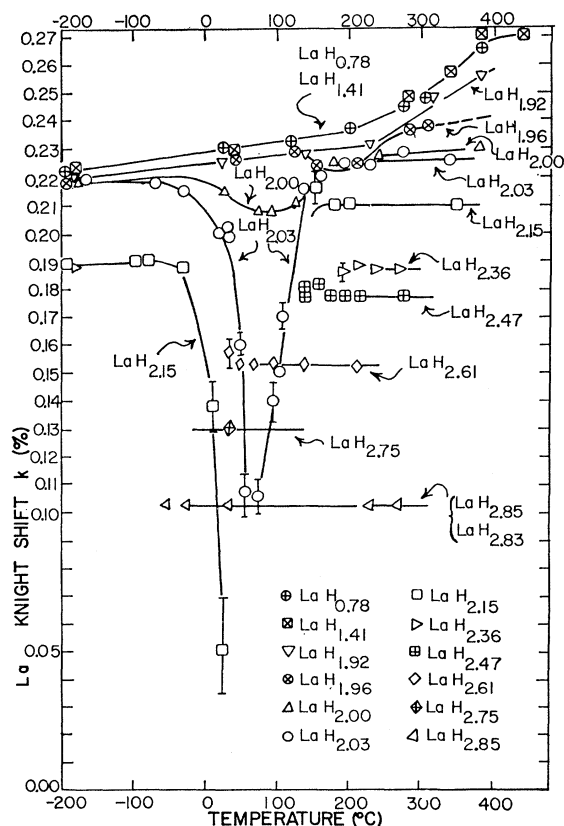

FIG. 14. Temperature dependence of lanthanum resonance shift for concentrations ranging from 0.78 H/La to 2.85 H/La.

instead of the segregated two-phase system that exists at low T. As is observed in Fig. 13, the Knight shift increases with decreasing H concentration so that by extrapolating back for the concentrations with greater than 2H/La into the deficient region, such an increase could be expected.

Outside of the observation of a general correlation between K and magnetic susceptibility, the extent of each of the various contributions of χ to K is not clear at this time, except that $C_3\chi_{\text{orb}}$ may be as large as $C_1\chi_s+C_2\chi_d$ as evidenced by the La T_1 data.

C. Concluding Remarks

Both lanthanum and hydrogen NMR measurements confirm the existence of a separated two-phase system in LaH_x, $x<1.94$. The resonance characteristics are independent of concentration in this region and the lanthanum resonance of both phases are observable. The fact that the hydride change in characteristics occurs at a value of about 1.94 instead of 2.00 is typical of other metal hydrides and implies an inaccessibility of 0.05 La tetrahedral sites.

It is interesting to note that the quadrupole couplings are unusually short ranged, about half a lattice con-

FIG. 13. Concentration dependence of lanthanum Knight shift recorded at 400°C.

stant, and that use of a Mott screening constant seems appropriate.

There is little indication that the octahedral sites remain occupied for any appreciable length of time in the deficient ($x<1.94$) concentrations. The hydride lanthanum resonance shows no quadrupolar effects, even as the protons start to diffuse. One can conclude, using a typical quadrupolar interaction as $\omega_{Q0} \approx 3 \times 10^6$ sec^{-1}, that the lifetime of a diffusing proton in an octahedral site in $x<1.94$ concentrations must be considerably less than 10^{-7} sec at temperatures greater than 300°C where diffusion is evident. Diffusion-dependent quadrupolar effects exist only in concentrations with $x>2$ and are consistent with a treatment of the occupied octahedral site as a point defect.

The vanishing Knight shift of the proton resonance and the ease of diffusion of protons are not incompatible with the model of a positive hydrogen ion or proton.[36] We assume that the electron from the hydrogen is ionized to the conduction band localized on the La

ions. This picture is consistent with the susceptibility and conductivity data if the conduction band, part of the $6s-5d$ bands of La, becomes filled when 3H/La are added. Martin and Rees[19] have suggested a similar band-structure for Zr-H. It is here suggested that in La-H the $5d$ band of La is *split* into two bands in which the lower energy band can accommodate four electrons. A maximum of about four electrons in the lower part of the d band is consistent with the maximum solubility of hydrogen in the other group IIIB to VB transition metals.

ACKNOWLEDGMENTS

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Empirical Analysis of the H⁻ Photodetachment Cross Section*

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The zero-range photoelectric cross section of Bethe and Peierls, corrected according to effective range theory, is fitted to the H⁻ photodetachment cross section. The value of 2.64 a_0 obtained for the effective range agrees with values obtained from the wave-function calculations of Schwartz, Burke and Schey, and others. A more accurate formula for the detachment cross section is obtained by allowing for distortion in the final p state by means of an approximate formula for the phase shift. This formula agrees qualitatively with the close-coupling theory phase-shift results of Burke and Schey, and provides a photodetachment cross section that fits the experimental data slightly better than the results recently obtained by Geltman with an elaborate variational treatment. There are two adjustable parameters: the binding energy, and one parameter in the phase-shift formula. By a slightly different choice of the parameters than is required to fit the experimental data, close agreement can also be obtained with the Geltman results.

I. INTRODUCTION

SINCE the original suggestions of Wildt[1] concerning the importance of H⁻ photoabsorption in stellar atmospheres, much effort has gone into the calculation of H⁻ wave functions and the H⁻ photodetachment cross section. Since the early estimates[2] of the photodetachment cross sections were not very satisfactory, Chandrasekhar undertook a series of increasingly more elaborate

calculations.[3] He used successively better variational bound-state functions, with a plane-wave continuum function and with more accurate versions that allowed for distortion.

In 1956, Geltman[4] obtained a usefully accurate representation of the H⁻ photodetachment cross section by means of a very simple model. He obtained both bound- and free-state wave functions for a cutoff Coulomb potential, and computed the cross section from these. Since then, renewed effort has been spent in obtaining

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