

## Diffusion & Electronic Parameters of $\text{LaNiInH}_x$ systems

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**Abstract:**  $^1\text{H}$  cw and pulsed NMR studies done in order to study the electronic & diffusion parameters, reveal that  $\text{LaNiInH}_x$  with  $x = 1.0, 1.36$  &  $1.55$  are single-phased both with respect to crystal structure and hydride formation whereas  $\text{LaNiInH}_{0.45}$  is double-phased with respect to hydride formation though single-phased crystallographically. The electron density of state at the Fermi surface does not vary appreciably with  $x$ . The activation energy for proton motion increases with the increase in  $x$ .

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### 1. Introduction

The study of electronic structure & hydrogen diffusion in the hydrides of  $\text{Fe}_2\text{P}$  type [1]  $\text{RNiX}$  system ( $\text{R} = \text{Th, La, Ce, Y}$  etc and  $\text{X} = \text{Al, In}$  etc.) reveals that the diffusion of hydrogen in these compounds are quite complex. For example, the activation energies obtained for  $\text{CeNiAlH}_x$  [2],  $\text{ThNiAlH}_x$  [3] &  $\text{YNiAlH}_x$  [2] are approximately 1.7, 2.6, 5.1 kcal/mol respectively. There is a wide fluctuation not only in these parameters but also in the other diffusion and electronic parameters. The reasons for such wide fluctuations in the iso-structural compounds, on the basis of electronic and magnetic structure, are not yet established.

In this paper, we report the study on an iso-structural compound,  $\text{LaNiInH}_x$  ( $x = 0.45, 1.0, 1.36$  &  $1.55$ ) having no localized electronic spin, proton - proton interaction and the proton - conduction electron interaction only being

effective in causing relaxation of the protons. Both the  $^1\text{H}$  cw NMR and pulsed NMR studies have been done on the system by means of which various electronic and diffusion parameters have been obtained.

## 2. Experimental

$\text{LaNiIn}$  and its hydrides were prepared as in ref. 4. The samples were characterised by XRD studies and magnetic susceptibility measurements. The samples are found to be single phased hydrides free of any paramagnetic impurities. The cw signals were taken in the frequency range 6 - 35 MHz and at temperatures 100 - 400 K. The  $^1\text{H}$  spin-lattice relaxation time ( $T_1$ ) was measured in the temperature range 140 - 420 K at 90 , 40 & 12 MHz using the inversion recovery ( $180^\circ - \tau - 90^\circ$ ) pulse technique. Due to low S/N ratio, data could not be taken at low temperatures for 12 MHz.

## 3. Results & Discussions

**$^1\text{H}$  cw NMR Studies:** A single resonance line was obtained in the entire range of 100 - 420 K for higher concentration of hydrogen i.e.  $x = 1.0, 1.36, \& 1.55$ . This confirms that the hydrides at these concentrations are all formed in a single phase. In contrast,  $\text{LaNiInH}_{0.45}$  shows a composite line consisting of a broad and a narrow line in the intermediate range of 250 - 385 K. The two components correspond to the two phases, one of which corresponds to the metal - hydrogen solution and the other is hydride phase where both the phases have the same crystallographic structure. The width for the broader line shows appreciable temperature dependence, whereas the narrow line shows almost temperature independent behaviour.  $^1\text{H}$  resonance line-width as a function of temperature has been plotted for all the hydrogen concentrations of  $\text{LaNiInH}_x$  as shown in figure 1. A static lattice line of width  $\sim 10$  Oe is observed around 200 K and below for hydrogen concentrations,  $x = 1.36 \& 1.55$  whereas for  $x = 0.45 \& 1.0$  the width is  $\sim 6$  Oe. This indicates that the two different types of lattice sites are occupied by the protons in the two cases.

The gradual broadening of the resonance line with the decrease in temperature can be understood in terms of a diffusion process of the hydrogen which when considered, allows a large portion of the nuclear dipole - dipole interac-

tion to be averaged out by the motion of proton with a consequent narrowing of the observed line-width. The temperature dependence of the correlation time for the proton magnetic dipole interaction is found by fitting the line-width ( $\delta H$ ) against temperature plots to the theory of Kubo & Tomita [5]. This fit is applied in the high temperature limit where  $\tau_d$ , the correlation time, is much less than the proton spin-spin relaxation time  $T_2'$  and in this regime it is of the form [3]

$$\delta H = [\gamma(\delta H_o)^2 / (2\sqrt{3})] \tau_{do} \exp(E_a / KT) \quad (1)$$

where  $E_a$  is the activation energy required for the motion of the proton,  $\tau_{do}$  is the pre-exponential factor and  $\delta H_o$  is the peak-to-peak separation of the absorption derivative of the rigid-lattice resonance line. Eqn. 1 is fitted to the observed  $\delta H$  for each concentration ( $x$ ) of hydrogen and the values of  $E_a$  and  $\tau_d$  thus determined are listed in table 1. To understand the detailed nature of motion,  $^1\text{H}$  spin-lattice relaxation studies have been performed.

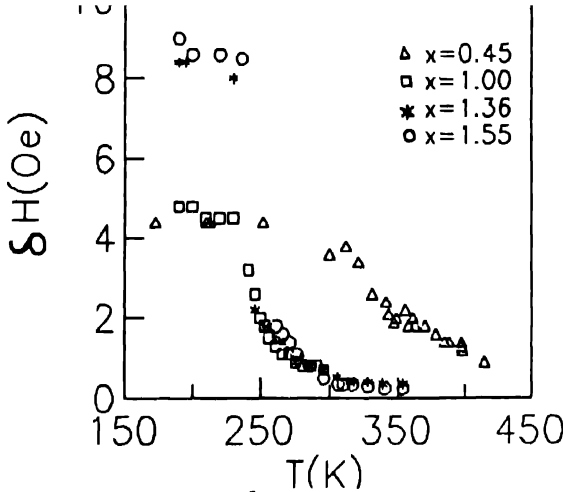


Fig. 1. Plots of line-width  $\delta H$  of  $^1\text{H}$  cw NMR lines against temperature for  $\text{LaNiInH}_x$  at  $\nu_o = 15$  MHz.

**Spin-lattice relaxation studies:** For all the concentrations, except  $x = 0.45$ , the resonance spectra show the existence of a single line throughout the temperature range. Decay of the magnetization with delay time  $\tau$  follows exponential behaviour at high temperature. However, the non-linearity in the initial part of the decay process for all the concentrations at all the frequencies

has been observed most distinctively in the low temperature regime. The non-linear part which occurs at the low values of the delay time  $\tau$  does not follow the  $\tau^{1/2}$  law [6], which is valid if paramagnetic impurity is present. Hence the non-linearity due to the presence of the paramagnetic impurity is ruled out.

The two regions showing two types of slopes were tried to be fitted by two independent values of relaxation times  $T_1$ , say  $T_{1a}$  and  $T_{1b}$  for all the concentrations throughout the temperature range, at all the frequencies. However, no such fit was possible indicating the absence of two independent relaxation modes having different  $T_1$  values. Nevertheless, the values of  $T_1$ 's are obtained from the linear portion of the decay processes.

Experimental  $T_1$  values thus obtained are plotted as  $\ln T_1$  vs  $1/T$  as shown in figures 2 & 3, at a particular frequency of 90 MHz and hydrogen concentrations of  $x = 0.45, 1.0, 1.36$  &  $1.55$  in the former and at a concentration  $x = 1.55$  and frequencies 90, 40 & 12 MHz in the latter.

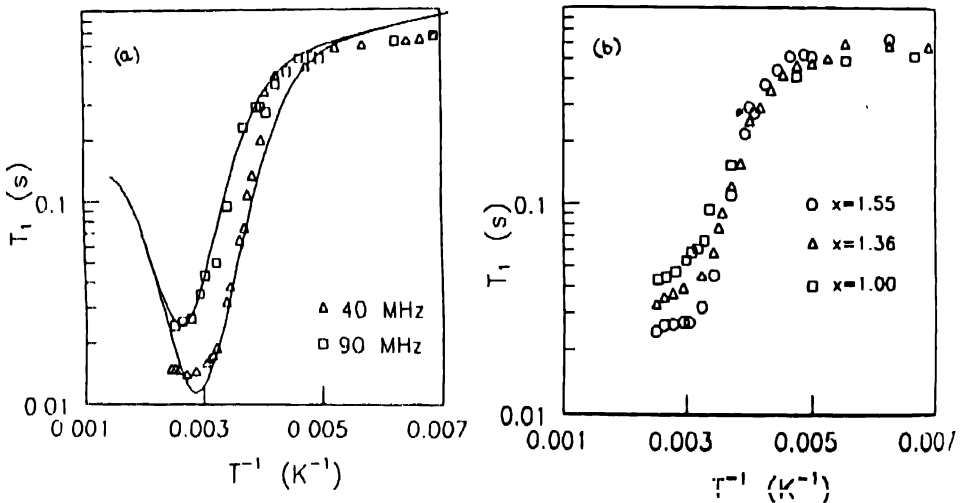


Fig. 2 (a): Plots of  $^1H$  spin-lattice relaxation  $T_1$  against inverse of temperature  $T^{-1}$  for  $LaNiInH_{1.55}$  at  $\nu_o = 40$  and 90 MHz. Continuous lines are the fitted lines to eqn. 2. (b): Plots of  $T_1$  for  $LaNiInH_x$  against  $T^{-1}$  at  $\nu_o = 90$  MHz.

The plots reveal that there is a considerable temperature dependence of the spin-lattice relaxation time ( $T_1$ ) on temperature above  $\sim 260$  K for all the concentrations of hydrogen as in fig. 2(a) and at all the three frequencies for a particular concentration of the hydride as in the fig. 2(b). Also, it is

distinctly revealed from the two figures that the  $T_1$  has both concentration and frequency dependence in the high temperature regime. With the assumption that

$$T_1^{-1} = T_{1d}^{-1} + T_{1e}^{-1} \quad (2)$$

where  $T_{1d}^{-1}$  is the relaxation rate of the protons because of the modulation of the proton dipolar interactions due to the hydrogen diffusion through the lattice and  $T_{1e}^{-1}$  is that due to the interactions of the protons with the unpaired conduction electrons at the Fermi level. Starting at around 420 K, the rapidly rising portion of  $T_1$  is a characteristic of a diffusionaly dominated relaxation mechanism. The flattening out portion of the  $T_1$  curve at lower temperature reveals the growing importance of the conduction-electron contribution where the diffusional contribution is negligible.

The electronic contribution is proportional to the temperature and is independent of the resonance frequency i.e.  $1/T_{1e} = CT$  where  $C$  is the Korringa constant. The motional contribution to the relaxation rate  $T_{1d}^{-1}$  represented by  $T_{1d}^{-1}$ , according to Bloembergen-Purcell-Pound approximation, is given by

$$1/T_{1d} = (4M_2/(3\omega))[y/(4 + y^2) + y/(1 + y^2)]$$

where  $y = \omega\tau_d$  and  $M_2$  is the 'rigid lattice' second moment of the proton NMR line H-H dipole interactions. The experimental datas were fitted in the equation (2) and they fitted well as shown in fig. 2 yieding the values of  $C$ ,  $M_2$ ,  $\tau_{do}$  and  $E_a$  all of which excepting  $M_2$  have been listed in table 1. The line-width  $\delta(H)$ , obtained from  $M_2$  is tabulated in the table.

Sample	Pulsed NMR studies					cw NMR studies			
	$\nu_o$ MHz	$C$ ( $\times 10^{-3}$ $s^{-1}K^{-1}$ )	$E_a$ $\frac{eV}{atom}$	$\tau_{do}$ $\times 10^{-13}$ (s)	$\delta H$ (Oe)	$\nu_o$ MHz	$\delta H$ (Oe)	$E_a$ $\frac{eV}{atom}$	$\tau_{do}$ $\times 10^{-10}$ (s)
LaNiInH <sub>1.55</sub>	90	7.8	.24	12.0	11.6	15	10.0	.23	5.2
	40	8.6	.27	9.9	10.3				
LaNiInH <sub>1.36</sub>	90	9.3	.23	12.7	9.5	15	9.0	.19	42.0
LaNiInH <sub>1.00</sub>	40	11.7	.175	4.71	7.0	15	6.0	.18	11.5
LaNiInH <sub>0.45</sub>	40	10.5	.147	12.3	7.5	15	5.0	.15	—

Table 1 : Parameters obtained from  $^1\text{H}$  cw & pulsed NMR studies for  $\text{LaNiInH}_x$ .

The value of  $C$  is proportional to the density of electrons at the Fermi level i.e.  $N_d(E_f)$ , shows no variation indicating that the electron density at

the Fermi surface does not vary appreciably with the hydrogen concentration in the system.

The activation energy/atom i.e.  $E_a$  obtained for each concentration of hydrides from both the cw NMR and the pulsed NMR measurements are within the limits of error. With the decrease of the hydrogen concentration the activation energy decreases. This increase of mobility of the protons with the decrease in hydrogen concentration is very likely since the availability of lattice sites increases. Though this observation should have been reflected in the  $\tau_{do}$  values, the increasing mobility of hydrogen in the metallic lattice with the decreasing concentration of hydrogen in the system is not seen in the correlation time  $\tau_{do}$  obtained from cw NMR studies and the pulsed NMR studies. The order of magnitude varies with the measurement technique though the the order of magnitude for the four hydrogen concentrations are in conformity with each other for a particular technique of measurement, as is seen in the table. However, the exact values of  $\tau_{do}$ 's are not systematic even for a particular technique of measurement. All these are due to the fact that a slight error in the activation energy introduces considerable error in the correlation time.

## References

- [1] A. E. Dwight, M. H. Mueller, R. A. Conner, Jr., J. W. Downey & H. Knot, *Trans. Metall. Soc. AIME* **242**, 2075 (1968).
- [2] B. Bandyopadhyay, K. Ghoshray, A. Ghoshray & N. Chatterjee, *J. Phys : Condens. Matt.* **2**, 1253, (1990).
- [3] O. J. Zogal, D. J. Lam, Z. Zygmunt, H. Drulis, W. Petrynski & S. Stalinski, *Phys. Rev.* **B29**, 4837 (1984).
- [4] K. Ghoshray, B. Bandyopadhyay, Mita Sen, A. Ghoshray & N. Chatterjee, *Proc. of the SSP Symposium (Tirupati, India, 1992)*, *ibid. Phys. Rev.* **B47**, 8277, (1993).
- [5] R. Kubo, K. Tomita, *J. Phys. Soc. Jap.* **9** 888 (1954).
- [6] W. E. Blumberg, *Phys. Rev.* **119**, 79, 1960.