

Proton NMR in $\text{CeNiInH}_{0.53}$ down to liquid helium temperature

R RAY, A GHOSHRAY, K GHOSHRAY and N CHATTERJEE

S.S. and M.P. Division, Saha Institute of Nuclear Physics, 1/AF Bidhan Nagar, Calcutta 700 064, India

Email: agr@cmp.saha.ernet.in

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Abstract. The NMR probe and the matching network has been designed for the ^1H NMR study in $\text{CeNiInH}_{0.53}$ down to liquid helium temperature using Bruker MSL 100 spectrometer. NMR line-shape measurement shows the absence of any signature of proton pairing in $\text{CeNiInH}_{0.53}$ down to 3.86 K, as it was observed for high hydrogen concentration. The measurement of the spin-lattice relaxation time in the temperature range 300–20 K reveals that the relaxation rate is mainly governed by the Korringa-type relaxation mechanism.

Keywords. NMR; line shape; spin-lattice relaxation.

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1. Introduction

The evidence of an ordered arrangement of proton pairs with H–H separation ~ 1.5 – 1.6 Å, as found in Fe_2P type intermetallic hydrides CeNiInH_x and PrNiInH_x ($x \geq 1$) [1, 2] from NMR, has attracted much interest. Such type of pairing of protons with separation 1.9 Å has recently been observed by Kumitomo *et al* [3] in the sodium insertion compound of hydrogen molybdenum bronze. These results violate Switendick's criterion – the nearest neighbour H–H distance in a metal lattice has never been found to be less than 2.1 Å. However, the discovery of the stable bonding neutral dihydrogen molecules to molybdenum and tungsten complexes by Kubas *et al* [4] has led to the speculation regarding the possibility for two hydrogen atoms in bulk metal hydride to favour either a molecular form of pairing or a pairing of the two hydrogen atoms mediated by a metal atom [5].

In this paper, we report on ^1H NMR studies on $\text{CeNiInH}_{0.53}$ in the temperature range 3.8–70 K. Our earlier measurements above 77 K show that in CeNiInH_x with $x < 1.0$, protons do not exist in pairs and they are highly mobile in the interstices. The possibility of pairing of protons as mentioned above even in $\text{CeNiInH}_{0.53}$ at low temperatures, wherein hydrogens are supposed to be in rigid condition in comparison with NMR frequency, has led us to do this measurement. Results, however, indicate that there is no such type of pairing of protons in this compound even at liquid helium temperature. Nevertheless, the variation of spin-lattice relaxation time, T_1 with temperature (20–300 K) throw some light on the behaviour of f electron of the cerium ion in the compound.

Before describing the results in § 3, we indicate in § 2, the indigenous development of the NMR probe in some detail. Discussion of the resonance line-shape for two closely spaced protons (expected line-shape for paired protons in hydrides) in a polycrystalline sample has been made in subsection 3.1 of § 3 which describes results and discussion.

2. Experimental details

The sample we are using now is the one that we have used earlier. It was kept in a sealed quartz tube filled with argon. We have started the experiment by checking with the NMR and magnetization data and comparing with the earlier data. Magnetization measurement is specially important because, in these samples one can not rule out the possibility of the precipitation of nickel from the hydride. Even a slight precipitation of nickel would act as ferromagnetic impurity.

The relevant physical parameters of $\text{CeNiInH}_{0.53}$ which are thought to be essential for clarity of reading, are repeated here. Even after the hydrogenation, the system has been found to be a Fe_2P type compound having a hexagonal closed packed symmetry with $a = 7.57 \text{ \AA}$ and $c = 4.01 \text{ \AA}$. Moreover, the effective moment of a magnetic ion, μ_{eff} , in terms of Bohr magneton per formula unit and the paramagnetic Curie temperature θ are close to that of the parent compound CeNiIn which are 1.73 and -57 respectively [6].

2.1 Construction of NMR probe

We have constructed a NMR probe for measurements on a solid sample in a continuous flow cryostat for liquid helium. The NMR probe consists of a resonating coil with a suitable matching network for impedance matching of the transmitter and the pre-amplifier. Except the probe assembly we have utilized all other parts of our Bruker MSL 100 spectrometer.

One significant complication when doing NMR in a low temperature environment is the necessity of using a length of coaxial cable ($\sim 1 \text{ m}$) between the coil and the electronics outside the cryostat. One has two choices; either put the entire tank circuit in the bottom of the cryostat, or include the coax as a part of the tank circuit. The primary advantage of having the entire tank circuit cold is that one can obtain much higher Q's, which can substantially improve the signal to noise for narrow lines. Having the tank in the cryostat forces one to work at a fixed frequency, where both the frequency of operation of the tank and the quality of the match to 50 ohms are likely to change upon cooling down. Single frequency operation is avoidable if one is willing to design into the cryostat the necessary linkage to room temperature that would permit varying the tank tuning while cold. While this can be done it is by no means simple.

The choice of allowing the coax to be included in the tank circuit allows one to vary the frequency of operation: however, analysis of the tank circuit performances is complicated. In particular, the effect of the coax typically cannot be modeled by the addition of simple lumped circuit elements, such as its capacitance to ground. Transmission line properties of the coax must be included. The coil in the cryostat will have its impedance transformed by the coax. The transformed impedance of the coil at the top of the cryostat

may be inductive or capacitive, so that the tuning elements may include inductors as well as capacitors.

Developing the impedance matching network [7] requires that one is able to measure the impedance that the coax and coil present at the top of the cryostat. Bridges for just this purpose exist, however, they are reasonably expensive. Here, we generally take the help of a tuner unit of preamplifier units of MSL 100 spectrometer which behaves like a “magic T” in the front end. The “magic T” takes a signal from the source and splits it into two arms, one of which has a 180° phase shift. One of this arm is connected to the tank circuit (which has to be tuned to 50 Ω); and other to an rf terminator of 50 Ω impedance. Half of the power reflected from the arms is summed and appears at the output. Because of the 180° phase shift, the amount of the drive signal that gets to the output is due to the difference in the power reflected from the tank and from the terminator side. By trimming the condenser one can have a reasonable good match of 50 Ω.

Matching networks. There are ways of changing the impedance of resonant circuits to some desired value. Consider the parallel tank circuit [7] for which the impedance at resonance is $\sim \omega^2 L^2 / R = \omega L Q$. The combination of L and C can be chosen at a given frequency to get a desired impedance but sometimes there are constraints which will not allow a free choice of L and thus $L\omega Q$. A common (and easiest to implement) way to transform the impedance of a parallel tank circuit in such cases is to add a series capacitor. The resonance condition is very close to $\omega^2 L(C + C') = 1$, which is a familiar one with C replaced by $C + C'$. The impedance at resonance is still $\omega^2 L^2 / R$, as in the parallel tank, but the new L will be smaller than the old by a factor $1 + (C/C')$. Therefore, the new impedance will be smaller than the old by $[1 + (C/C')]^2$.

2.2 Cryostat

We have used a top loading continuous flow cryostat CF1200 of Oxford Instruments. A simple arrangement has been made to hold the cryostat in the yoke of Varian's 15" electromagnet model No. V7400. Provisions are also made to keep the sample portion of the cryostat in a region of maximum homogeneity of the magnetic field. This is generally done by monitoring the intensity of a narrow NMR line. The sample is cooled by conduction through helium gas in the sample space. The flow of liquid which cools the cryostat does not come into direct contact with the sample. The liquid is supplied from a separate storage vessel through an insulated transfer tube; it flows through a heat exchanger around the sample space, and out of the cryostat to the pump. A thermometer and heater are mounted on the heat exchanger and these are used with a temperature controller ITC503 of Oxford Instruments to balance the cooling power of the cryogen and to control the temperature of the heat exchanger. With this arrangement we have been able to maintain a temperature of 3.8 K.

The temperature at the sample site could be monitored by two sensors placed in contact with the NMR coil enclosing the sample. A platinum sensor and a silicon diode sensor were fixed at the two ends of the sample by Apiezon N greeze. There is absolutely no temperature difference between the two ends in the temperature range 20–60 K and this is within ± 0.1 K of the set temperature recorded by the sensor placed in the heat exchanger of ITC503. However, below 20 K, we had to use only the diode sensor.

3. Results and discussion

3.1 Resonance line-shape

The close proximity of two protons as for example in a water molecule of hydration in a crystal, results in a characteristic NMR line-shape [8]. This is a consequence of the strong dipolar interaction between the two protons. The Hamiltonian for such a spin pair in a strong applied magnetic field H_0 is given by

$$\mathcal{H} = -\gamma\hbar H_0(I_z^1 + I_z^2) + \frac{\gamma^2\hbar^2}{2r_{12}^3} [3(1 - 3\cos^2\theta)I_z^1I_z^2 - (1 - 3\cos^2\theta)\mathbf{I}^1 \cdot \mathbf{I}^2]. \quad (1)$$

Here, θ is the angle between the applied field H_0 and the vector r_{12} joining the two spins. Because of the perturbing term (second part of the Hamiltonian) the resonance line get splitted into two lines. These two resonance lines appear at

$$\nu_{\pm} = \nu_0 \pm (3\gamma^2\hbar/16\pi^2r_{12}^3)(3\cos^2\theta - 1). \quad (2)$$

For a single crystal, the separation of these two resonances from the unperturbed position ν_0 is a function of the angle θ . For a polycrystalline sample, the crystallites are oriented at all possible θ . The intensity pattern for the two transitions can be obtained as

$$I_{\pm}(\nu') = \int_{-\infty}^{\infty} P(\nu) \exp[-(\nu_{\pm} - \nu')^2/2\omega^2] d\nu, \quad (3)$$

where, $P(\nu)$ is the distribution function and is expressed as $P(\nu) \propto \int_0^{2\pi} \int_{-1}^1 (d(\cos\theta)/d\nu) d\phi$, $\exp[-(\nu_{\pm} - \nu')^2/2\omega^2]$ expresses the component line with ω as the root-mean-square deviation of frequency from the Larmor frequency.

In figure 1, computer generated line-shapes expected from the dipolar interaction between a close pair of protons with different proton-proton spacing (r_{12}) are shown. It is

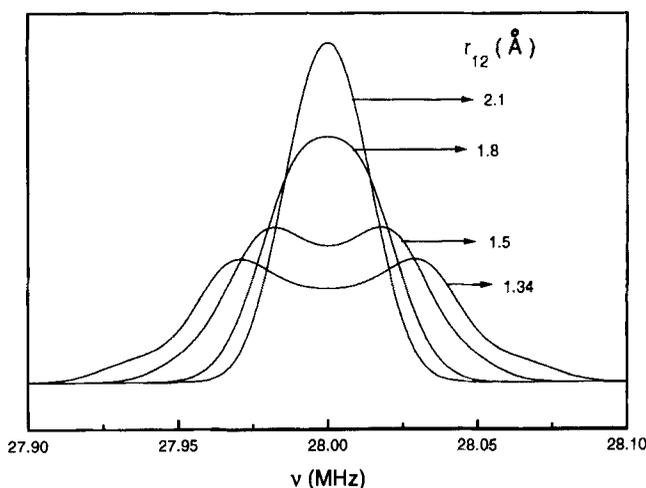


Figure 1. The theoretically generated line-shapes expected from the dipolar interaction between a close pair of protons with different proton-proton separation (r_{12}).

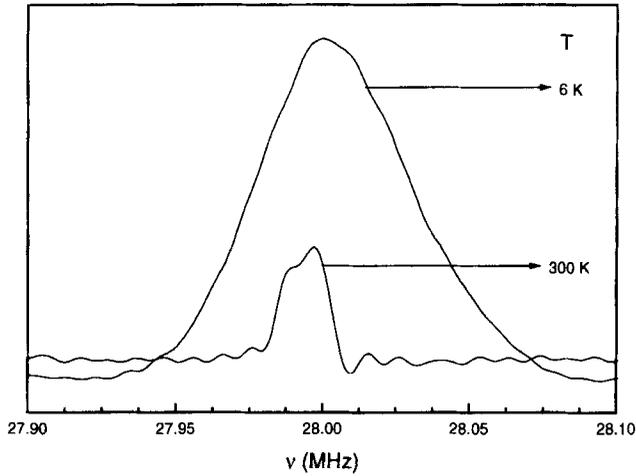


Figure 2. The experimental line-shape of ¹H NMR in CeNiInH_{0.53} at 300 K and 6 K. The spectra were obtained at 28 MHz using solid-echo pulse sequence (90° – τ – 90°).

clear from the figure that when the proton–proton spacing is less than 2.1 Å line-shape shows a characteristic Pake doublet pattern, whereas, if the protons are randomly distributed throughout the interstitial sites the resonance line-shape will not display the doublet-peak structure characteristic of the strong dipolar interaction.

A comparison of the observed proton resonance in CeNiInH_{0.53} at 6 K and 300 K as shown in figure 2, with the theoretically generated line-shape reveals that the ¹H–¹H separation in CeNiInH_{0.53} is not less than 2.1 Å i.e. the protons in CeNiInH_{0.53} are not in the paired state down to 3.86 K. As the temperature is decreased down to 3.86 K the line-width ($\delta\nu$) of the NMR line-shape get increased. The temperature variation of $\delta\nu^{-1}$ shows that the line-width of the NMR line-shape is almost governed by the broadening due to susceptibility.

3.2 Spin-lattice relaxation time

We consider that the measured spin-lattice relaxation rate T_1^{-1} over the temperature range investigated (300–20 K) arises from three contributions

$$T_1^{-1} = (T_1)_K^{-1} + (T_1)_{RKKY}^{-1} + (T_1)_{d,ce}^{-1} \quad (4)$$

where, $(T_1)_K^{-1}$ is the conduction electron contribution which follows the Korringa relation $(T_1)_K^{-1} = C_K T$. $(T_1)_{d,ce}^{-1}$ is the dipolar coupling of proton to the electronic magnetic moment of each Ce³⁺ ion. $(T_1)_{RKKY}^{-1}$ is due to the interaction between the proton and the localized *f* electron through the conduction electrons.

The ¹H spin lattice relaxation time T_1 has been measured at 28 MHz using inversion-recovery (180° – τ – 90°) technique. The spin-lattice relaxation rate, T_1^{-1} of proton in CeNiInH_{0.53} as a function of temperature is shown in figure 3. T_1^{-1} does not show significant variation in the temperature range 300–225 K. Below 225 K, relaxation rate T_1^{-1}

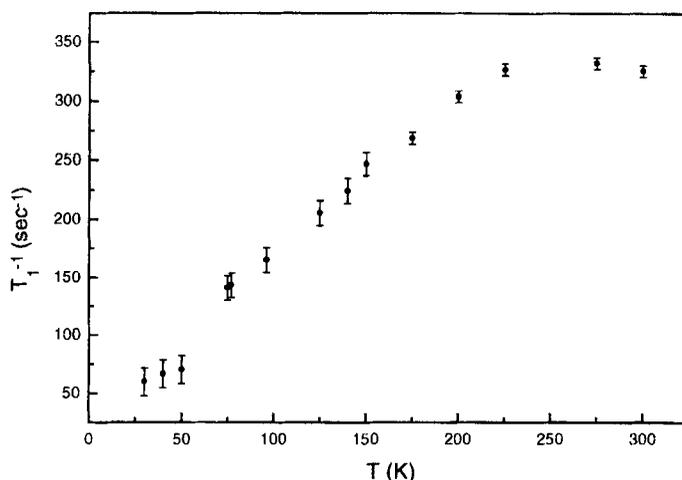


Figure 3. The temperature variation of spin-relaxation rate (T_1^{-1}) of proton in $\text{CeNiInH}_{0.53}$ in the temperature range 300–20 K.

decreases linearly with the lowering of temperature. This indicates that in the temperature range 225–20 K the relaxation mechanism is dominated by the Korringa-type relaxation mechanism and there is no effect of any localized magnetic moment. This observation suggests the complete delocalization of $4f$ electron of Ce ion. Here it is to be mentioned that in case of other rare earth ternary intermetallic hydrides such as CeNiAlH_x and CeCuAlH_x [9], the proton spin-lattice relaxation mechanism is dominated by the influence of localized magnetic moment of Ce^{3+} ion through the RKKY interaction mechanism.

4. Conclusion

Protons do not exist in pairs in case of $\text{CeNiInH}_{0.53}$ even at 4 K. The spin-lattice relaxation rate (T_1^{-1}) in the temperature range 20–225 K follows Korringa behaviour. This is in sharp contrast with the observation made in CeNiAlH_x and CeCuAlH_x , wherein the effect of f -electron dominates the relaxation mechanism.

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Proton NMR in CeNiInH_{0.53}

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