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Observation of a Pake doublet in the ^{1}H nuclear-magnetic-resonance spectrum of $CeNiInH_x$

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^{1}H nuclear-magnetic-resonance (NMR) studies have been performed in $CeNiInH_x$ ($x=1.0$ and 1.6) in the temperature range 140–300 K. Near 300 K, the ^{1}H NMR spectra show a single narrow line. Below about 210 K, the spectra look very much like a Pake doublet on which a central narrow line is superimposed. The experimental ^{1}H NMR spectrum of $CeNiInH_{1.0}$ at 140 K has been fitted to a theoretical line shape consisting of a doublet and a central Lorentzian line. This fitting yields a proton-proton separation of about 1.48 Å±0.02. The ordered arrangement of the paired protons in CeNiIn has been discussed in terms of the proposed hydrogen sites in isostructural systems.

The discovery of stable bonding of neutral dihydrogen molecules (H_2) to molybdenum and tungsten complexes by Kubas *et al.* in 1983 (Ref. 1) has led to the speculation regarding the possibility for two hydrogen atoms in a bulk metal hydride to favor either a molecular form of pairing or a pairing of the two hydrogen atoms mediated by a metal atom. The possibility of occurrence of paired hydrogen atoms in bulk hydride was considered as a mechanism to explain the anomalous behavior of proton (^{1}H) and deuterium (^{2}D) spin-lattice relaxation rates T_1^{-1} at very high temperature observed in many systems: $NbH_{0.2}$, $VH_{0.2}$, $YH_{1.9}$, $TaH_{0.3}$, $ZrH_{1.8}$, $YD_{1.9}$, $ScD_{1.9}$, and $Nb_{0.5}V_{0.5}H_{0.36}$.[2]

In all cases, T_1^{-1} were found to increase markedly with temperature in the range 700–1000 K. Such a relaxation behavior could not be explained by mechanisms, such as, interaction of nuclei with conduction electrons, fluctuation of nuclear dipolar interaction due to the motion of interstitials, and the presence of paramagnetic impurities. A simple model was developed by Cotts[3] assuming that relaxation occurs in some excited state in the bulk hydrides. If this state were a pairing state, H-H spacing would need to be less than that in the normal H_2 molecule. Moreover, the lifetime for the formation of H_2 molecules would have to be as large as 300–1000 times the normal mean residence time of hydrogen. The more recent measurement[2] of proton relaxation data in $Nb_{0.5}V_{0.5}H_{0.36}$ clearly reveals that the decrease of the correlation time τ_c with the increase of temperature must be associated with the increase of the mean-square magnetic-field fluctuation M_2 of the H-H interaction. Thus it may be presumed that the pairing would be a dynamic process with a relatively short lifetime equal to the measured correlation time $\tau_c=3\times10^{-9}$ s.

Even before the discovery by Kubas *et al.*, the proposition of pairing of hydrogen atoms in metal hydrogen systems had been put forward by Bonnet, Juckum, and Lucasson[4] in 1982 in order to explain the anomalous temperature-dependent behavior of the resistivity differences between yttrium metal and a solid solution (α phase) of hydrogen or deuterium with yttrium in the atomic concentration (x) range 0.05–0.24. The added resistivity due to H (or D) interstitials displayed a minimum at around 170 K which, as they proposed, marked the occurrence of a reversible transition between a particular paired configuration of H (or D) interstitials and a random distribution of single interstitials. Also it was proposed that most of the pairing configuration would be along the c direction of the hcp lattice where the two nearest-neighbor tetrahedral sites are separated by 1.35 Å. Such a pairing of the hydrogen atoms should result in the appearance of a characteristic Pake doublet in the ^{1}H NMR line shape in α-YH_x because of negligible line broadening due to the neighboring metal nuclei (^{89}Y-^{1}H dipolar interaction is much weaker than ^{1}H-^{1}H interaction). However, the search for such a doublet yielded negative result.[5] Though the static response of ^{1}H spins have failed to show any evidence of hydrogen pairing in metal hydrides, study of proton dynamics, however, indicates the evidence of short-range hydrogen pairing occurring in some systems.

For example, the measurements of (T_1) of proton in α phase Sc-H, Y-H, and Lu-H systems in the temperature range 10–120 K (Ref. 6) exhibit a peak in T_1^{-1} corresponding to fast localized motion of hydrogen between the closely spaced tetrahedral sites (separated by ~1.35 Å). It is interesting to note that the frequency and temperature dependence of the T_1^{-1} peak exhibited characteristics typical of the amorphous and disordered systems suggesting the formation of hydrogen pairs with little long-range order resulting effectively in a "proton glass."

Recent diffuse neutron-scattering measurements[7] in these systems have revealed the existence of short-range order which has been modeled by zig-zag chains formed by "H-metal atom-H" arrangements along the c axis. The modulated ridges of diffuse scattering intensity that reveal this essentially one-dimensional order, persist even to room temperature; while at low temperatures, diffuse scattering peaks appear, which indicates the onset of three-dimensional short-range order, apparently involving interchain interactions.

In metal hydrogen systems, therefore, any of the following types of hydrogen-hydrogen pairing may be expected: (a) pairing of two H atoms bonded to metal atoms, in this case H-H separation would be about 1.4 Å, and (b) molecular bonding of two H atoms.

In this paper, we report the ^{1}H NMR results in $CeNiInH_x$ ($x=1.0$ and 1.6). In these systems the ^{1}H resonance spectra below about 240 K, clearly show the resonance line shapes characteristic of a Pake doublet. This result gives a direct experimental evidence of the pairing of hydrogen atoms with a long-range order in a metal-hydrogen system.

The compound CeNiIn was prepared by repeated arc melting of the constituent elements on a water-cooled copper hearth under argon atmosphere. The samples, wrapped in tantalum foils, were annealed at 700 °C for 72 h in vacuum and subsequently, were characterized by x-ray powder-diffraction studies. The hydrogenation procedure was similar to that reported earlier.[8] The hydrogenated samples, prepared in equilibrium condition, were kept in argon filled sealed glass tubes. The ^{1}H NMR studies were performed in a Bruker MSL100 pulse spectrometer using a Varian V7400 electromagnet.

In the temperature range 140–300 K, the magnetic susceptibility of CeNiIn exhibits a weak temperature dependence.[9] In case of CeNiInH$_{1.0}$ and CeNiInH$_{1.6}$, however, the susceptibility is strongly temperature dependent and it increases with decrease in temperature. In case of NMR, the ^{1}H resonance linewidth in solids is primarily determined by the proton-proton dipolar interaction. However, an inhomogenous broadening of the linewidth due to the bulk magnetization of the sample may also be present. This extra broadening is proportional to the susceptibility and also to the applied magnetic field. In order to keep this broadening at a minimum and that also without considerably hampering the signal-to-noise ratio, the experiments have been performed at low resonance frequencies, viz., 8–34 MHz. It is observed that the overall features of the resonance line shape, as described below, do not vary in this region of frequencies. To overcome the problem of instrumental dead-time delay, in case of broad lines, the solid echo sequence (90°-τ-90°) was used. However, the spectra obtained from free-induction-decay signal and that from spin-echo, showed negligible difference in spectral features.

At room temperature and down to 273 K, the spectra (Fig. 1) appear as a single narrow and asymmetric line. Interestingly, near 260 K, there appear two peaks symmetrically disposed on both sides of the central line. With lowering of temperature, the intensities of the two new peaks are found to increase, while that of the central line decreases. The spectra at 210 K and below, look very much like a Pake doublet on which a central narrow line is superimposed. Figure 1 shows that the positions of the peaks remain more or less unchanged upon variation of temperature. The effect of bulk sample magnetization on the linewidth has been illustrated in Fig. 2, in which ^{1}H NMR spectra of CeNiInH$_{1.0}$ at 140 K and at the resonance frequencies of 12.0 and 34.0 MHz have been shown. The figure shows that the central line as well as the two outer peaks are somewhat broadened at 34.0 MHz. Still, the positions of the peaks do not change significantly from those at 12.0 MHz. The ^{1}H spectrum of CeNiInH$_{1.6}$ at 12.0 MHz and at 140 K has also been shown in Fig. 2. The shape of the resonance line and also the separation of the peaks are similar to those of CeNiInH$_{1.0}$. In this context, it may be pointed out that the ^{1}H

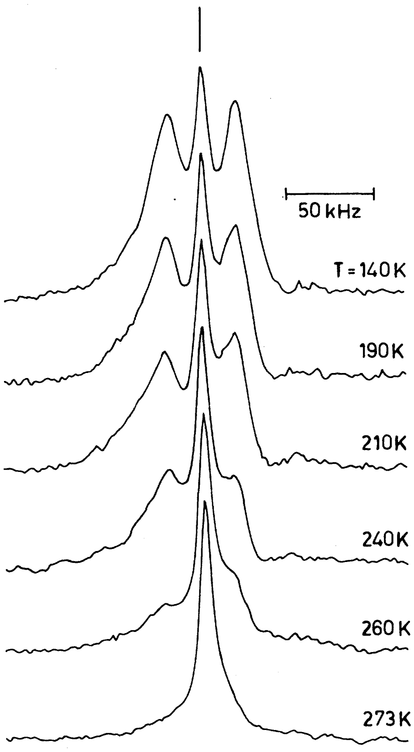

FIG. 1. ^{1}H NMR spectra of CeNiInH$_{1.0}$, at a resonance frequency of 12.0 MHz and at different temperatures. The signal gains have not been normalized. The vertical line at the center indicates the position of ^{1}H resonance in pure water taken as the reference.

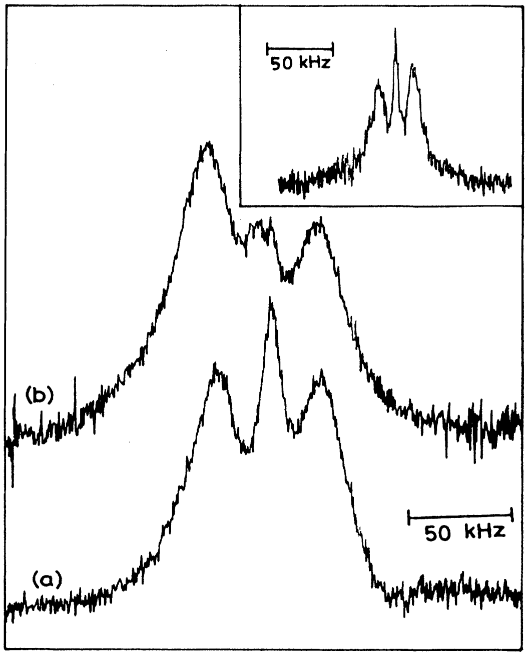

FIG. 2. ^{1}H NMR spectra of CeNiInH$_{1.0}$ at 140 K and at the resonance frequencies (a) 12.0 MHz, and (b) 34.0 MHz. Inset shows the ^{1}H resonance spectrum of CeNiInH$_{1.6}$ at 12.0 MHz and at 140 K.

NMR spectra in the hydrides of isostructural CeNiAl exhibited[10] only the superposition of a broad and a narrow components at certain temperature regions depending upon hydrogen concentrations. It is worthwhile to mention that a narrow central component superposed on a broad pairlike background has been observed in $PdH_{0.82}$ system.[11] Surprisingly, no detailed interpretation of the broad feature was attempted though it was suggested that the overall background is due to homogeneous broadening arising from hydrogens located at chemically inequivalent sites.

Such a line shape with three peaks may be observed also in case of a system of three identical spin-$\frac{1}{2}$ nuclei at the corners of an equilateral triangle, as in 1,1,1,-trichloroethane.[12] The possibility of such a situation has been excluded considering the following observation. We have obtained a number of spectra using the 180°-τ-90° pulse sequence with varying delay times τ. Figure 3 shows some of the spectra obtained at a resonance frequency of 12.0 MHz and at 170 K. It is observed that the zero magnetization (which corresponds to condition $\tau = T_1 \ln 2$) corresponding to the two outer peaks occurred simultaneously at a time $\tau = 80\ \mu s$, while that corresponding to the central peak occurred much later, at $\tau = 1$ ms. Thus, the protons corresponding to the two outer peaks seem to exhibit identical T_1, which is at least an order of magnitude shorter than the T_1 of protons corresponding to the central peak. From this observation it can be suggested that the protons corresponding to both the outer peaks are in a particular type of interstitial site, which is different from the site of protons corresponding to the central peak. The facts that ^1H nuclei corresponding to the two outer peaks exhibit similar spin-lattice relaxation time and that the two outer peaks are positioned symmetrically on the two sides of the reference position (i.e., the position of ^1H resonance in pure water), strongly suggest that these two peaks constitute a doublet as was first observed by Pake[13] in dihydrated calcium sulphate. An attempt has been made to fit the experimental line shape (^1H resonance spectrum of $CeNiInH_{1.0}$ at 12 MHz and at 140 K) to a double-peak structure accompanied with a central line represented by the equation[13]

$$I(\nu) = \int_{-\infty}^{\infty} p(\nu') s(\nu - \nu') d\nu' + I_L(\nu) , \qquad (1)$$

where $p(\nu')$ is the probability distribution function for the powder sample line shape expected from the dipolar interaction between a close pair of protons, and is defined as

$$p(\nu') \sim \begin{cases} (\nu'/\alpha + 1)^{-1/2} \\ \text{between } \nu' = -\alpha \text{ and } \nu' = 2\alpha \\ + (-\nu'/\alpha + 1)^{-1/2} \\ \text{between } \nu' = -2\alpha \text{ and } \nu' = \alpha , \end{cases}$$

where $\alpha = \frac{3}{2}\mu^2 r^{-3}$, in which μ is the magnetic moment and r is the proton-proton separation. The component line has been assumed to be a Gaussian and is given by $s(\nu - \nu') = \exp[-(\nu - \nu')^2 / 2\beta^2]$ in which β is the root-mean-square deviation of frequency from the Larmor value. The line shape for the central line may be assumed to possess the characteristic of a dilute random distribution of spins, i.e., a Lorentzian shape given by, $I_L(\nu) \propto 1/(1 + 4\nu^2/\beta'^2)$, in which β' is the linewidth at half-maximum.

With these assumptions the best fitted curve is shown by the broken line in Fig. 4. The amplitudes of the doublet and the central line have been adjusted to match the theoretical fit with the experimental line shape. It is seen that the fitted curve reasonably agrees with the experi-

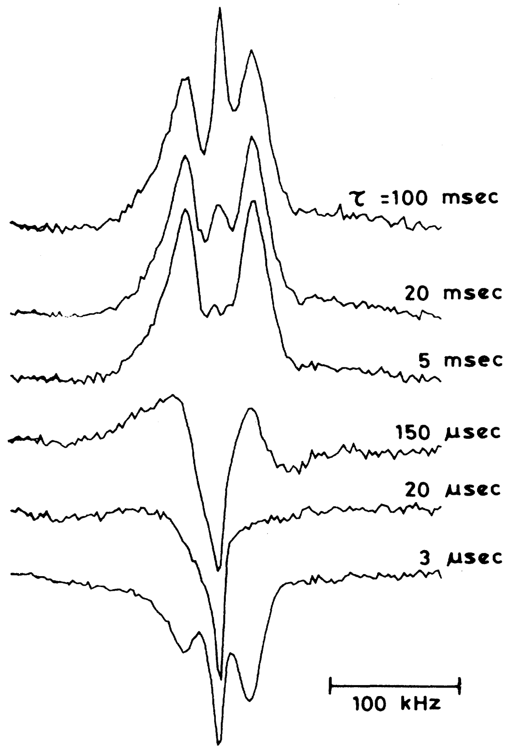

FIG. 3. ^1H NMR spectra of $CeNiInH_{1.0}$ at 170 K and at a resonance frequency of 12.0 MHz, obtained using the inversion-recovery (180°-τ-90°) pulse sequence in which τ is the variable delay time.

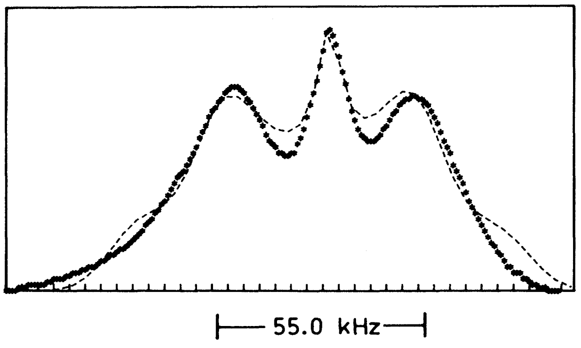

FIG. 4. Comparison of ^1H NMR spectra of $CeNiInH_{1.0}$ at a resonance frequency of 12.0 MHz and at 140 K (represented by * marks) with the theoretical fit to Eq. (1) (broken line).

mental line shape except that the characteristic steps at the wings of a Pake doublet are not visible in the spectrum, possibly because of the magnetic broadening present in the spectrum. The parameters obtained from the fitting are $2\alpha=(55\pm2)$ kHz and $\beta=6.65$ kHz. From the value of α, the proton-proton separation r has been estimated to be (1.48 ± 0.02) Å

It has been shown[14] that in ANiAl (A =Zr,Y,U) type of compounds, the most favorable sites of hydrogen occupation are (a) $6i$ tetrahedral sites composed of three A atoms and one aluminum atom $(0.29, 0, \frac{1}{3})$; (b) $4h$ tetrahedral sites composed of three A atoms and one Ni(I) atom $(\frac{1}{3},\frac{2}{3},\frac{1}{3})$; and (c) $12l$ tetrahedral sites composed of two A atoms, one aluminum atom, and one Ni(I) atom $(0.44, 0.16, \frac{2}{9})$. For isostructural CeNiIn, the corresponding sites are $6i$(3Ce+1In), $4h$[3Ce+1Ni(I)], and $12l$[2Ce+1In+1Ni(I)]. The shortest $4h$-$4h$ and $6i$-$6i$ distances occur along the c axis of the hexagonal structure. Using the lattice parameters of CeNiIn, these distances have been estimated to be 1.32 Å. However, upon hydrogenation of CeNiIn, its lattice parameters, and so also the separation between the interstices, may be slightly modified.

The observation of a Pake doublet in the ^{1}H NMR in $\mathrm{CeNiInH}_{1.0}$ therefore suggests that in CeNiIn, the hydrogen atoms may occupy the nearest-neighbor tetrahedral sites separated by about 1.4 Å, resulting in a periodic arrangement of paired protons.

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[1] G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini and H. J. Wasserman, J. Am. Chem. Soc. **106**, 451 (1984).

[2] D. B. Baker, N. Adolphi, M. S. Conradi, P. A. Fedders, R. E. Norberg, R. G. Barnes, and D. R. Torgeson, Phys. Rev. B **46**, 184 (1992), and references therein.

[3] R. M. Cotts, J. Less-Common Met. **172-174**, 467 (1991).

[4] J. E. Bonnet, C. Juckum, and A. Lucasson, J. Phys. F **12**, 699 (1982).

[5] L. Lichty, R. J. Schoenberger, D. R. Torgeson, and R. G. Barnes, J. Less-Common Met. **129**, 31 (1987).

[6] R. G. Barnes, J. Less-Common Met. **172-174**, 509 (1991).

[7] O. Blaschko, J. Less-Common Met. **172-174**, 237 (1991).

[8] B. Bandyopadhyay, A. Ghoshray, and N. Chatterjee, Bull. Mater. Sci. **9**, 305 (1987).

[9] H. Fujii, T. Inoue, Y. Andoh, T. Takabatake, K. Satoh, Y. Maeno, T. Fujita, J. Sakurai, and Y. Yamaguchi, Phys. Rev. B **39**, 6840 (1989).

[10] B. Bandyopadhyay, K. Ghoshray, A. Ghoshray, and N. Chatterjee, Phys. Rev. B **46**, 2912 (1992).

[11] S. R. Kreitzman and R. L. Armstrong, Phys. Rev. B **25**, 2046 (1982).

[12] H. S. Gutowsky and G. E. Pake, J. Chem. Phys. **18**, 162 (1950).

[13] G. E. Pake, J. Chem. Phys **16**, 327 (1948).

[14] S. Biderman, I. Jacob, M. H. Mintz, and Z. Hadari, Trans. Isr. Nucl. Soc. **10**, 129 (1982).