

^1H nuclear-magnetic-resonance study of CeNiAlH_x and CeCuAlH_x

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(Received 11 September 1991; revised manuscript received 13 March 1992)

^1H cw and pulsed NMR studies on the hydrides CeNiAlH_x , with hydrogen concentration $0.09 \leq x \leq 2.85$ and CeCuAlH_x with $x=0.64$ and 1.51 have been performed in the temperature range 100–400 K. In all samples, the ^1H spectra appear as a broad resonance line at low temperatures, a narrow resonance line at high temperatures, and a superposition of a narrow component and a broad component at intermediate temperatures. The temperature dependence of the linewidth of the narrow component indicates the presence of mobile hydrogen. The activation energy of hydrogen motion in $\text{CeNiAlH}_{2.85}$ has been estimated to be $E_a = 1.7$ kcal/mol. Measurement of the spin-lattice relaxation time T_1 of protons reveals the coexistence of two types of ^1H nuclear magnetizations at all hydrogen concentrations. In one type (in the case of CeNiAlH_x), which makes the dominant contribution to the total magnetization, the relaxation mechanism is dominated by the influence of localized magnetic moments, whereas the other type present in small proportion is characterized mainly by a Korringa-type relaxation mechanism. The results thus suggest that hydrogenation of CeNiAl leads to the formation of a two-phase compound. In one phase, i.e., the hydride phase, hydrogenation results in the transformation of the Ce^{4+} state to the Ce^{3+} state. This hydride phase contains two types of hydrogen sites; hydrogen atoms in one of the sites are mobile resulting in a narrow line. The second phase contains a cerium ion in the Ce^{4+} state, as in the parent compound CeNiAl ; this phase may be the solid-solution phase of CeNiAl and hydrogen. In the case of CeCuAl , there is no hydrogen-induced valence transformation, and cerium is in the Ce^{3+} state in CeCuAl as well as in its hydrides. It is found that in CeCuAlH_x there are also two types of ^1H nuclear magnetization, but in this case the relaxation behavior of both magnetizations are influenced by localized magnetic moments. These results have been analyzed by considering contributions from different mechanisms to the relaxation process, e.g., (a) a contact interaction between the conduction electrons and the proton, (b) the Ruderman-Kittel-Kasuya-Yosida interaction between the proton and the localized f electron through the conduction electrons, and (c) a dipolar interaction between a proton and Ce^{3+} localized magnetic moments.

I. INTRODUCTION

A recent magnetization measurement in CeNiAl and its hydrides, CeNiAlH_x (x is the number of hydrogen atoms/formula unit) indicated that the $4f$ electron, which was completely delocalized in CeNiAl , became localized after charging CeNiAl with hydrogen to form CeNiAlH_x .¹ Specifically it may be mentioned that the cerium ion exists in the Ce^{4+} state in CeNiAl ,¹ whereas in CeNiAlH_x with $x \geq 1.5$ it exists in the Ce^{3+} state with an effective moment μ_{eff} , close to that of the free Ce^{3+} ion. In the CeNiAlH_x samples with $x \leq 1.5$ it has been observed that the magnetization increases with increasing hydrogen concentration. These results indicated that hydrogenation modifies the band structure of CeNiAl in such a way that the overlapping of the $4f$ level with the conduction band is reduced. In particular, hydrogenation of CeNiAl affects the valence state of cerium in the same way as when cerium is alloyed with copper instead of nickel forming CeCuAl .¹ That the cerium ions tend to be in the $4+$ state in CeNiAl also follows from a comparison of the lattice constants in the series $R\text{NiAl}$ (R = rare earth).²

Hydrogen-induced changes in the valency of the cerium ions have also been observed by Buschow³ in the

study of the magnetic properties of CeCo_3 , Ce_2Co_7 , and CeNi_3 and their ternary hydrides. CeCo_3 and CeNi_3 are Pauli paramagnetic, whereas Ce_2Co_7 is ferromagnetic with $T_c = 50$ K. The hydrides CeCo_3H_4 and $\text{Ce}_2\text{Co}_7\text{H}_7$ exhibit ferromagnetism with $T_c = 80$ and 233 K, respectively. Though no magnetic ordering is observed in CeNi_3H_3 , the effective moment is found to be $2.5\mu_B$ (Ce atom)⁻¹. The changes in the magnetic properties have been ascribed to a change in the valency of the cerium ions (from $4+$ to $3+$).

The microscopic mechanism that is responsible for this sort of hydrogen-induced valence transformation has not yet been the subject of extensive theoretical and experimental investigations. In this paper, we would present the results of a systematic ^1H NMR studies in CeNiAlH_x system. Since NMR is a local probe, the effect of localized $4f$ electron coming from the cerium ion would be manifested both in the time-averaged and time-dependent resonance parameters. For comparison, the corresponding observation of ^1H NMR in the CeCuAlH_x system, where there is no hydrogen-induced transformation of the valence state of cerium^{1,2} would also be performed. These results have been compared with those of ^1H NMR in CeH_x , where no hydrogen-induced valency transformation of Ce^{3+} ion was observed.

II. EXPERIMENTAL

The method of sample preparation and its hydrogenation has been described earlier.¹ For NMR studies fresh samples have been prepared and characterized by x-ray diffraction studies and magnetization measurements. ^1H NMR measurements have been performed on the CeNiAlH_x ($x=0.09, 0.27, 0.56, 0.83, 1.32, 1.8, 2.14,$ and 2.85) and CeCuAlH_x ($x=0.64$ and 1.51) systems. CeNiAl absorbs a large amount of hydrogen even at low equilibrium pressures. Thus, it has not been possible to prepare all the samples at equilibrium conditions except for $x \geq 1.8$.

All ^1H NMR data were taken by using either the cw method in field-sweep mode or the pulse method. The cw measurements were made with a Varian WL210 spectrometer in the frequency range 6–35 MHz and in the temperature range 100–400 K. For pulsed measurement a Bruker MSL100 spectrometer combined with a Varian electromagnet V7400 was used. The ^1H spin-lattice relaxation time T_1 was measured in the temperature range 140–300 K at 40 MHz using inversion-recovery ($180^\circ\text{-}\tau\text{-}90^\circ$) technique. In the case of a broad line, the solid-echo sequence ($90^\circ\text{-}\tau\text{-}90^\circ$) was used as a monitoring pulse and thus the complete pulse sequence was $180^\circ\text{-}\tau\text{-}90^\circ\text{-}\tau_1\text{-}90^\circ\text{-}\tau_2$ echo. From the change in magnetization $M(\tau)$ with the delay time τ obtained from the peak values of the Fourier-transformed signal taken at different τ values, T_1 was determined.

III. RESULTS AND DISCUSSION

A. Spectral features

^1H cw NMR spectra in CeNiAlH_x ($0.09 \leq x \leq 2.85$) and CeCuAlH_x ($x=0.64$ and 1.51) show a superposition of two lines having different linewidths, in certain temperature regions. The temperature regions in which the two components are observed, are different for different hydrogen concentrations. For example, a superposition of two components has been observed in the spectra of CeNiAlH_x system corresponding to concentrations $x \leq 1.32$ and $\text{CeCuAlH}_{0.64}$ at 300 K and at all temperatures down to 200 K. Below 200 K, however, the spectra appear as single broad lines. On increasing the temperature above 300 K, the intensity of the broad component gets reduced, while that of the narrow component is increased. Finally, at around 395 K, only the narrow component is observed. In samples of higher concentrations, i.e., for $x \geq 1.8$ in CeNiAlH_x and in $\text{CeCuAlH}_{1.51}$, the spectra at 300 K appear as single narrow lines. The superposition of two lines in these cases can be observed only in the spectra at lower temperatures, below about 250 K. The ^1H NMR spectra of $\text{CeNiAlH}_{2.85}$, as shown in Fig. 1, exhibit a single broad line at low temperature, a superposition of two components with different linewidths at intermediate temperatures, and a single narrow line at high temperature, as described above. It may be mentioned that in the case of hydrogenation of isomorphous YNiAl ,⁵ a single motionally narrowed ^1H resonance line was observed for YNiAlH_x with $x \leq 0.75$.

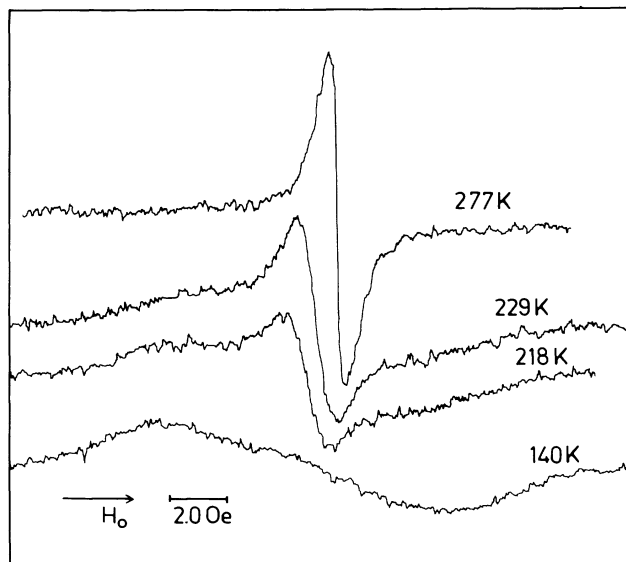


FIG. 1. ^1H cw NMR spectra of $\text{CeNiAlH}_{2.85}$ at different temperatures and at $\nu_R = 15$ MHz.

However, for $x \geq 0.75$, two proton resonances were found to coexist over a certain temperature interval.

B. Temperature dependence of linewidth

The temperature dependence in the linewidth may originate from either or both of (i) temperature-dependent bulk magnetic susceptibility χ for which the change in linewidth would be linear with χ , and (ii) the modulation of nuclear-nuclear dipolar interaction due to hydrogen mobility. However, it has been observed that linewidths of both narrow and broad components increase linearly with the applied field. To observe the effect of hydrogen motion on the linewidth, its temperature dependence was studied at a lower resonance frequency of 11.5 MHz. Also the signals in all cases were obtained with a modulation level less than one fifth of the width of the narrower component.

Figure 2 shows plots of linewidth versus temperature for the broad and narrow components in $\text{CeNiAlH}_{0.56}$ and $\text{CeNiAlH}_{2.85}$. Both components exhibit considerable broadening as the temperature is lowered and this effect is more pronounced in case of broad component. The inset of Fig. 2 shows the temperature dependence of linewidths for the broad and narrow components in CeCuAlH_x , exhibiting similar nature as shown by the linewidth of the CeNiAlH_x system.

The linewidth versus χ plots for the broad components in $\text{CeNiAlH}_{0.56}$ and $\text{CeNiAlH}_{2.85}$ are given in a Fig. 3(a). In both samples, the broad component exhibits same linearity with χ . This observation indicates that any motion of hydrogen atoms, if present in sites corresponding to the broad component, is sufficiently slow compared with the NMR frequency.

On the other hand, χ dependence of linewidth of the

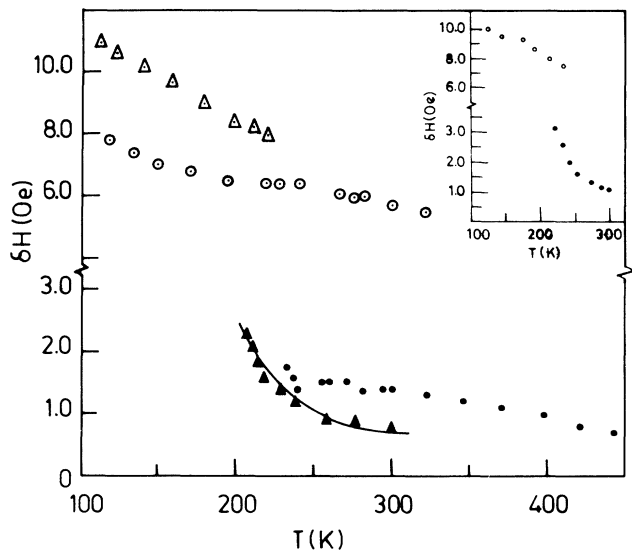


FIG. 2. Temperature dependence of linewidth δH of ^1H cw NMR lines of CeNiAlH_x system at $\nu_R = 11.5$ MHz. \bullet , narrow component: $x=0.56$; \blacktriangle , narrow component: $x=2.85$; \circ , broad component: $x=0.56$; and \triangle , broad component: $x=2.85$. Inset shows the same features for ^1H NMR lines at 8 MHz of $\text{CeCuAlH}_{1.51}$ system; \bullet , narrow component and \circ , broad component. The continuous line is a theoretical fit to Eq. (1).

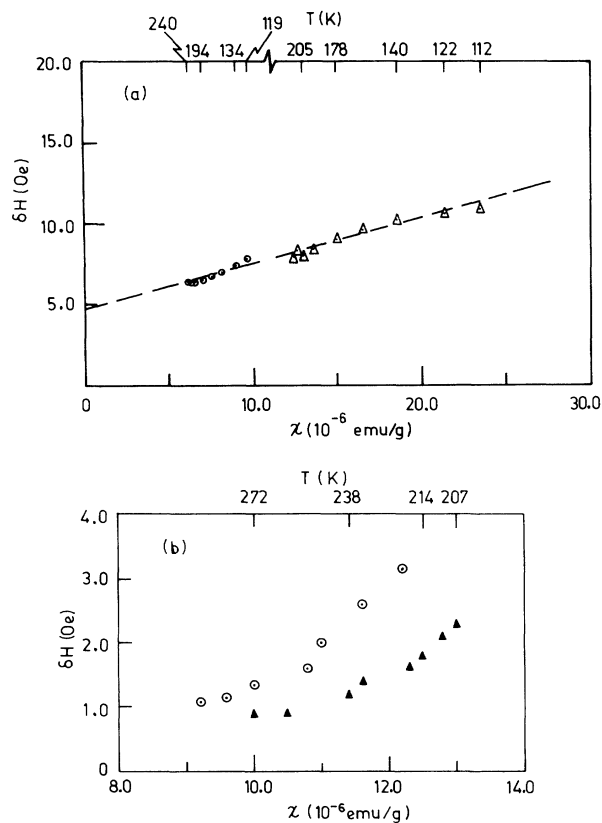


FIG. 3. Plots of linewidth δH of ^1H cw NMR lines in CeNiAlH_x against susceptibility χ . (a) Broad component: \circ , $\text{CeNiAlH}_{0.56}$; \triangle , $\text{CeNiAlH}_{2.85}$ and (b) narrow component: \blacktriangle , $\text{CeNiAlH}_{2.85}$; \circ , $\text{CeCuAlH}_{1.51}$.

narrow component in $\text{CeNiAlH}_{2.85}$ is not linear [Fig. 3(b)]. For comparison, variation of the linewidth of the narrow component of $\text{CeCuAlH}_{1.51}$ has also been shown. This indicates that the width of the narrow component, apart from being broadened due to the presence of localized magnetic moments, is further influenced by the motion of hydrogen atoms. Such a motion reduces the effect of nuclear-nuclear dipolar interaction and thus causes the motional narrowing of the NMR lines. An estimation of the activation energy E_a for hydrogen motion and the attempt frequency ν_0 may be made by fitting the observed variation of linewidth δH with temperature (Fig. 2) to the expression^{5,6}

$$\delta H = [\gamma(\delta H_0)^2 / (2\sqrt{3})] \nu_0^{-1} \exp(E_a / kT), \quad (1)$$

in which δH_0 is the rigid lattice linewidth (peak to peak separation of absorption derivative). In case $\text{CeNiAlH}_{2.85}$ such a fitting yields $E_a = 1.7$ kcal/mol and $\nu_0 = 1.9 \times 10^7$ Hz. Such a small value of activation energy may appear surprising as $E_a < 3.5$ kcal/mol is not generally observed in hydrides of intermetallic compounds.⁷ In the hydrides of YNiAl , the values of E_a were ~ 5 kcal/mol.⁵ As $\text{CeNiAlH}_{2.85}$ contains localized Ce^{3+} moments, the value of E_a , as estimated here, may be biased by a broadening of resonance line due to the higher value of bulk magnetic susceptibility. But it is to be noted that even with this magnetic broadening, the ^1H resonance linewidth in $\text{CeNiAlH}_{2.85}$ is much smaller than that in $\text{YNiAlH}_{1.17}$ (Ref. 5) in the motionally narrowed regime, even though the latter has a much smaller hydrogen concentration. This may be an indirect indication of a very high mobility of H atoms in $\text{CeNiAlH}_{2.85}$ so that the activation energy of motion could also be very small.

C. ^1H spin-lattice relaxation

1. CeNiAlH_x

Let us first discuss the spectral features obtained by inversion-recovery sequence. Figure 4 shows the spectra at various τ values for $\text{CeNiAlH}_{0.83}$ at 188 K. The spectra at $\tau = 80 \mu\text{s}$ and $\tau = 1.0$ s clearly show the existence of two components, as observed in the cw spectra. More significantly, however, the spectra at intermediate τ values show that, following the inversion, the broad component decays much sooner than the narrow component. At an intermediate τ value, $\approx 500 \mu\text{s}$, the magnetization corresponding to the broad component decays to almost zero, while that of the narrow component still exists in the inverted condition. This clearly demonstrates that the T_1 of the narrow component is much longer than that of the broad component. At all temperatures in the range 140–300 K, this sort of behavior of the magnetization of the different components are observed in all CeNiAlH_x with $x \leq 1.32$. At higher hydrogen concentrations $x \geq 1.8$, the inversion-recovery spectra near 300 K show only a single narrow line as observed in the cw spectra. Interestingly, the zero magnetization corresponding to this narrow line occurs at $\tau \approx 1$ ms. Thus the relaxation time, even for this narrow resonance line, is of

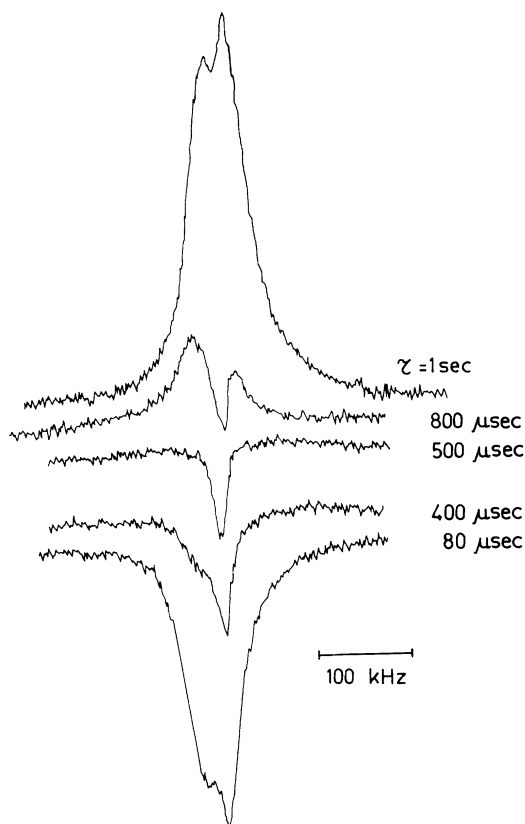


FIG. 4. ¹H Fourier transform spectra of CeNiAlH_{0.83} at 188 K obtained from inversion-recovery sequence at different delay times τ .

the same order of magnitude as that of the broad component of resonance line at lower hydrogen concentrations. Nevertheless, in these samples too, the decay of nuclear magnetization does not follow a single-exponential behavior, indicating the existence of another component of smaller magnitude, but having a longer T_1 . At lower temperatures, however, two distinct components with different T_1 , as obtained for $x \leq 1.32$, have been observed.

The spectral features thus suggest that at any hydrogen concentration, ¹H nuclear magnetization in CeNiAlH_x is composed of two types of contributions with different relaxation times. It was therefore assumed that the amplitudes of the spectra at different τ values, obtained in the inversion-recovery sequence, may be fitted with an equation,

$$M(\tau) = M_a [1 - 2 \exp(-\tau/T_{1a})] + M_b [1 - 2 \exp(-\tau/T_{1b})], \quad (2)$$

where M_a and M_b are supposed to be the equilibrium magnetization of the two components to which the relaxation times, respectively, T_{1a} and T_{1b} are associated, with the choice $T_{1a} < T_{1b}$. Thus by fitting the variation of magnetization $M(\tau)$ with τ values to Eq. (2), we obtain the relaxation rates T_{1a}^{-1} and T_{1b}^{-1} of two components and

their equilibrium magnetization, M_a and M_b , respectively.

In all samples it has been found that $M_a > M_b$ at all temperatures; i.e., the component of magnetization having shorter T_1 (i.e., T_{1a}) is always dominant in the spectra. This observation, together with the spectral features, therefore indicates that the component with shorter T_1 , depending upon hydrogen concentration and temperature, may appear either as a superposition of a broad and a narrow resonance lines or as a single narrow line or a broad resonance line. Over and above these, another component showing longer relaxation time (T_{1b}) may sometimes be present in the spectra. But as this component also exhibits a small linewidth, comparable to that of the narrow component with shorter T_1 , the former component cannot be distinguished from the latter in the cw spectra.

The variation of T_{1a} with temperature in CeNiAlH_x ($x=0.56, 1.32$, and 2.85) is plotted in Fig. 5. In CeNiAlH_{0.56}, T_{1a} does not show significant variation in the range 200–296 K. Below 200 K, it shows a decreasing tendency but the values obtained, as plotted in Fig. 5, become more and more uncertain as the temperature decreases. The reason for the uncertainty is that the spectra at these temperatures show very poor signal-to-noise ratio because of the low hydrogen concentration and line broadening. At higher hydrogen concentrations, however, T_{1a} clearly decreases with decreasing temperature. These results thus show that the ¹H spin-lattice relaxation mechanism in CeNiAlH_x is affected by the localized magnetic moments. The occurrence of trivalent cerium ions in the hydrides of CeNiAl, as observed from the magnetic susceptibility measurements, is therefore also reflected in the behavior of T_1 . Significantly, the nature of temperature dependence of T_{1a} does not vary appreciably upon a change in the hydrogen concentration, i.e., the ¹H nuclei are similarly influenced by the localized moments at all hydrogen concentrations.

The temperature-dependence behavior of T_{1b} is com-

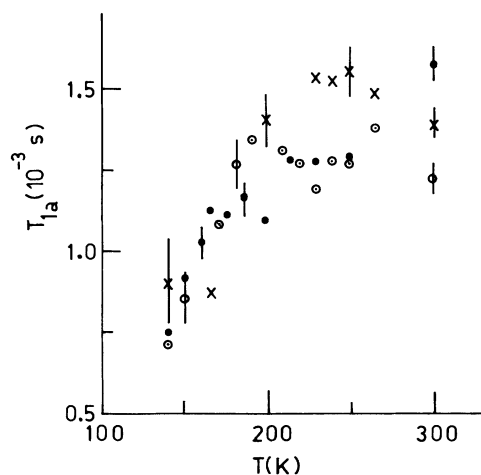


FIG. 5. Plot of ¹H spin-lattice relaxation time T_{1a} (as defined in the text), against the temperature at $\nu_R = 40.5$ MHz: \times , CeNiAlH_{0.56}; \circ , CeNiAlH_{1.32}; and \bullet , CeNiAlH_{2.85}.

TABLE I. The values of A , η , $\Theta(Q)$, and C_K for CeNiAlH_x and CeCuAlH_x systems.

Compound	A ($\text{s}^{-1} \text{K}$)	η (s^{-1})	$\Theta(Q)$ (K)	C_K ($\text{s}^{-1} \text{K}^{-1}$)	T_1 parameter
$\text{CeNiAlH}_{0.56}$				0.022	T_{1b}
$\text{CeNiAlH}_{1.32}$	4050	192	116	1.53	T_{1a}
				0.052	T_{1b}
$\text{CeNiAlH}_{2.85}$	2330	308	102	0.78	T_{1a}
				0.113	T_{1b}
$\text{CeCuAlH}_{0.64}$	27 700	664			T_{1x}
	636	120.7	109	1.27	T_{1y}

pletely different from that of T_{1a} . Figure 6 shows the plots of T_{1b} versus reciprocal temperature (T^{-1}) in CeNiAlH_x ($x=0.56, 1.32,$ and 2.85). In all samples T_{1b} decreases with increase in temperature and the decrease in T_{1b} is more pronounced in samples of low hydrogen concentration. However, very sharp decrease in T_1 , characteristic of rapid motion of H atoms, as was observed⁵ in the case of YNiAlH_x , could not be observed here. Measurements of T_1 at higher temperatures was not performed because it was observed that the error in estimation of T_{1b} was greater at higher temperatures due to the fact that at these temperatures the contribution of M_b becomes very small compared with M_a .

Below 200 K, T_{1b} slowly increases with decreasing temperature. This indicates that in a portion of the sample that is not influenced by the localized magnetic moments, the relaxation mechanism is dominated by the Korringa mechanism. From the linear plots of T_{1b} versus $1/T$ at these temperatures, the Korringa products $T_{1b}T$ have been estimated and are given in Table I. This product is found to decrease as the hydrogen concentration increases.

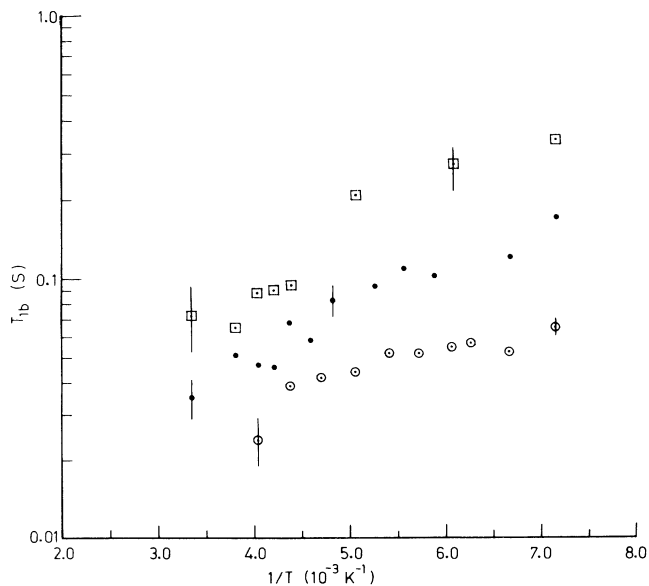


FIG. 6. Plot of ^1H spin-lattice relaxation time T_{1b} (as defined in the text), against inverse of temperature T^{-1} at $\nu_R=40.5$ MHz; \square , $\text{CeNiAlH}_{0.56}$; \bullet , $\text{CeNiAlH}_{1.32}$; and \circ , $\text{CeNiAlH}_{2.85}$.

2. CeCuAlH_x

The study of ^1H relaxation in $\text{CeCuAlH}_{0.64}$ shows that the decay of magnetization, in this case, can be well fitted with a form given by the sum of two components of magnetization M_x and M_y having different dynamic behavior [Eq. (2)]. The relaxation times associated with M_x and M_y have been designated as T_{1x} and T_{1y} respectively, with $T_{1x} < T_{1y}$. In this case also, the magnetization component having the shorter relaxation time (i.e., M_x with T_{1x}) has the dominant contribution in the total magnetization. Though T_{1y} is of same order of magnitude as T_{1a} (in CeNiAlH_x), T_{1x} and T_{1y} differ by at least an order of magnitude (Fig. 7). However, in this case, as the temperature is lowered, both T_{1x} and T_{1y} tend to decrease, indicating that in CeCuAlH_x the influence of the localized spin is dominant on the relaxation processes for both components of magnetization.

3. Contribution from different relaxation processes

We consider that the measured proton spin-lattice relaxation rate T_1^{-1} arises from three contributions

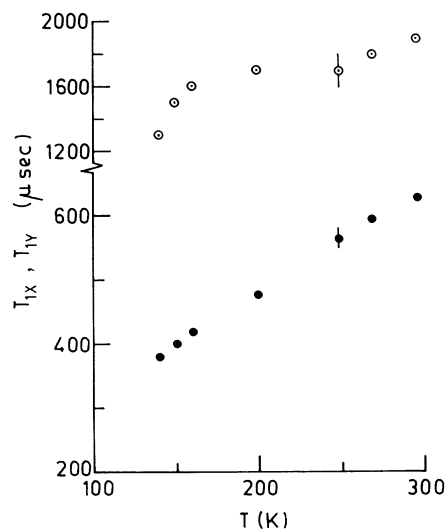


FIG. 7. Plot of ^1H spin-lattice relaxation time in $\text{CeCuAlH}_{0.64}$ at $\nu_R=40.5$ MHz. \bullet , T_{1x} and \circ , T_{1y} . T_{1x} and T_{1y} have been defined in the text.

$$T_1^{-1} = (T_1)_{d,Ce}^{-1} + (T_1)_K^{-1} + (T_1)_{RKKY}^{-1} . \quad (3)$$

$(T_1)_{d,Ce}^{-1}$ results from the dipolar coupling of proton to the electronic magnetic moment of each Ce³⁺ ion and is known to be⁸

$$(T_1)_{d,Ce}^{-1} \approx (\Delta\omega_{d,Ce})^2 \frac{\tau_c}{1 + \omega_I^2 \tau_c^2} , \quad (4)$$

where ω_I is the proton angular resonance frequency, τ_c is a correlation time characteristic of the proton-moment–Ce³⁺-ion-moment interaction, and $(\Delta\omega_{d,Ce})^2$ is the mean-square dipole-dipole interaction. In the range of temperature considered, τ_c is very small so that $\omega_I^2 \tau_c^2 \ll 1$. In addition, $\tau_c^{-1} = \tau_{e1}^{-1} + \tau_D^{-1}$, where τ_{e1} is the

ion spin-lattice relaxation time and τ_D is the correlation time for hydrogen diffusion. Since, in this case, $\tau_{e1} \ll \tau_D$, $\tau_c = \tau_{e1}$. Further, as τ_{e1} follows a Korringa-type behavior, i.e., $\tau_{e1} \propto 1/T$, we have from Eq. (4)

$$(T_1)_{d,Ce}^{-1} = A/T . \quad (5)$$

$(T_1)_K^{-1}$ is the Korringa relaxation rate and is given by

$$(T_1)_K^{-1} = \pi\gamma_I^2 \hbar k_B T H_{\text{hfs}}^2 N(E_F)^2 = C_K T . \quad (6)$$

$N(E_F)$ is the density of *s*-type electronic states per spin direction at the Fermi level and H_{hfs} is the hyperfine field at the nucleus.

$(T_1)_{RKKY}^{-1}$ is due to the interaction between conduction electrons and is given by⁹

$$(T_1)_{RKKY}^{-1} = (T_1)_K^{-1} \left[\frac{4N(E_F)(g_J - 1)^2 j(j+1) |J(Q)|^2}{3k_B [T - \Theta(Q)]} \right] = \eta \left[\frac{T}{T - \Theta(Q)} \right] , \quad (7)$$

where

$$\eta = 4\pi\gamma_I^2 \hbar k_B H_{\text{hfs}}^2 N(E_F)^3 |J(Q)|^2 (g_J - 1) j(j+1) / 3k_B ,$$

in which $J(Q)$ is the Q th Fourier component of the *s*-*f* exchange integral, Q being the critical wave vector spanning the nesting Fermi surface, j the total angular momentum of the localized electrons, g_J the Landé *g* factor, and

$$\Theta(Q) = -\lambda(Q)j(j+1) / (3k_B) ,$$

where $\lambda(Q)$ is the wave-vector-dependent constant of the molecular field. By comparing the magnetic susceptibility and T_1 data in some alloys and intermetallic compounds containing localized moments, Fradin⁹ has shown that a rough correspondence exists between $\Theta(Q)$ and the ordering temperature for compounds that exhibit either antiferromagnetic or ferromagnetic order at lower temperatures. However, there is no correspondence between the Curie-Weiss temperature, Θ , and $\Theta(Q)$ for those compounds that order antiferromagnetically. The behavior of $\Theta(Q)$ is an indicative of the fact that above the magnetic ordering temperature T_1^{-1} is influenced by the wave-vector-dependent correlations of the short-range magnetic order.

We performed a simplex type of fitting of the function

$$1/(T_1 T) = A/(T)^2 + \eta \left[\frac{1}{T - \Theta(Q)} \right] + C_K . \quad (8)$$

The computed best fit for T_{1a} in CeNiAlH_{1.32} and CeNiAlH_{2.85} and also for T_{1x} and T_{1y} in CeCuAlH_{0.64} are shown in Fig. 8. The values of the parameters obtained from the fitting are given in Table I. The values of A indicate that the dipolar contribution $(T_1)_{d,Ce}^{-1}$ is much smaller than that due to $(T_1)_{RKKY}^{-1}$ in all cases except for T_{1x} in CeCuAlH_{0.64}. The comparatively large value of A

in this case, however, is consistent with the fact that T_{1x} in CeCuAlH_{0.64} is considerably smaller than the T_{1a} in CeNiAlH_x.

$(T_1)_{d,Ce}^{-1}$ can be estimated from Eq. (4), provided that the hydride structure, the H-site occupancy, and the value of τ_{e1} are known. In the case of isostructural UNiAl, Biderman *et al.*¹⁰ suggested three types of favorable tetrahedral H sites whose equivalents in CeNiAl would be (i) 6i (3Ce+1Al), (ii) 4h (3Ce+1Ni_I), and (iii) 12l (2Ce+1Al+1Ni_I). Even if hydrogen atoms are assumed to occupy these sites, the lattice parameters of CeNiAlH_x and CeCuAlH_{0.64} and the value of τ_{e1} are unknown and therefore a reasonable estimation of $(T_1)_{d,Ce}^{-1}$ could not be done at this stage.

The values of C_K , i.e., the inverse of the Korringa product, indicate that on increase of hydrogen concentration, density of states at the proton site decreases, which is in agreement with our earlier susceptibility studies,¹ wherein a decrease in the Pauli spin susceptibility with increasing hydrogen concentration has been observed. Though, in case of CeNiAlH_x we find a large value of $\Theta(Q)$, there is no indication of magnetic ordering from the susceptibility study. In particular, the susceptibility follows a Curie law for all hydrogen concentrations in CeNiAlH_x.¹ Thus the argument in favor of some sort of correspondence,⁹ as mentioned earlier between $\Theta(Q)$ and the ordering temperature, does not hold good in the case of CeNiAlH_x. Further, in the absence of any knowledge of the Knight shift, the significance of the values of η could not be ascertained.

D. Coexistence of two resonances and comparison with other hydrides

¹H NMR in CeNiAlH_x and CeCuAlH_x exhibit a composite resonance spectra, showing a superposition of a broad component and a narrow component in certain

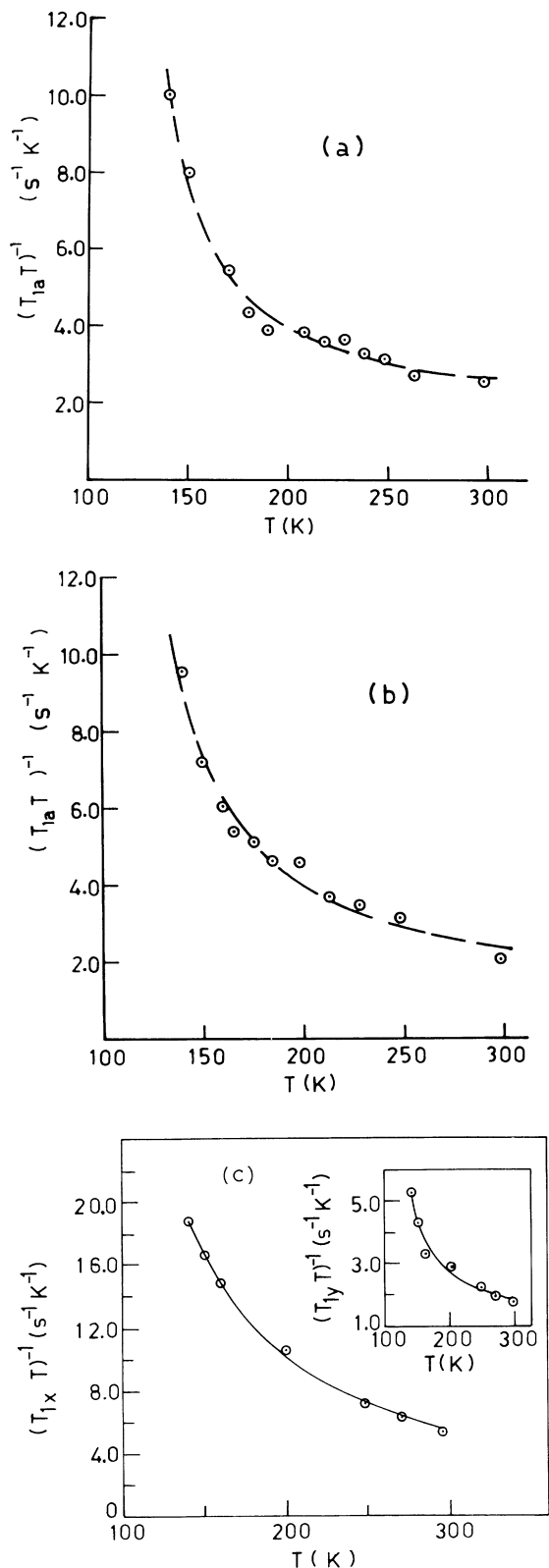


FIG. 8. Plot of $(T_1 T)^{-1}$ against temperature for dominating magnetization component of (a) $\text{CeNiAlH}_{1.32}$, (b) $\text{CeNiAlH}_{2.85}$, and (c) $\text{CeCuAlH}_{0.64}$. Inset in (c) shows the same for the smaller component of magnetization in $\text{CeCuAlH}_{0.64}$. The theoretical curve fitted to Eq. (8) has been shown in each case. T_{1a} , T_{1x} , and T_{1y} are defined in the text.

temperature intervals. Isostructural systems such as YNiAlH_x (Ref. 5) and ThNiAlH_x (Ref. 11) have also exhibited such a superposition of ^1H NMR lines. In the case of YNiAlH_x , the measurement of the ^1H spin-lattice relaxation time has revealed two components corresponding to H atoms located in two different sites and that the ^1H nuclei in these sites exhibit different motional behavior. However, in that case, the observation of a single relaxation behavior at lower temperatures has reflected a common electronic structure of the two types of sites in a single-phase hydride. In CeNiAlH_x also, the appearance of two components may indicate that H atoms occupy different type of sites in a particular phase. But in this phase, the ^1H relaxation mechanism at any site has a larger contribution from the interaction with paramagnetic Ce^{3+} ions compared with the contribution from the nuclear-nuclear dipolar interaction. Any difference in the latter due to a difference in hydrogen mobility at different sites is, therefore, not reflected in the total spin-lattice relaxation rate.

The above argument, however, does not rule out the possibility of coexistence of different phases. The influence of localized magnetic moment is so large that the differences in the ^1H relaxation behavior in these phases may not be resolved so that an overall relaxation rate is obtained. The similar arguments also hold good for the magnetization component M_x with a relaxation time T_{1x} in CeCuAlH_x .

In this connection, it may be mentioned that in CeH_x (Ref. 4) also, the ^1H resonance line showed a superposition of two components but only a single relaxation behavior was observed. Also it was shown that ^1H relaxation rate in both tetrahedral and octahedral sites was dominated by $(T_1)_{d,Ce}^{-1}$ [Eq. (5)]. In the present case, we have shown that the contribution of this term is much smaller than $(T_1)_{\text{RKKY}}^{-1}$, indicating that the electron-nuclear dipolar interaction in this case is not strong. Apparently the reason seems to be that, while in case of metallic cerium, the H atoms are surrounded by Ce^{3+} ions from all sides, in the case of CeNiAl and CeCuAl , one or two of the atoms constituting a tetrahedral site (6i, 4h, and 12l, as mentioned earlier), are diamagnetic.

IV. CONCLUSION

^1H NMR studies in CeNiAlH_x system with $0.09 \leq x \leq 2.85$ and CeCuAlH_x with $x = 0.64$ and 1.51 reveal the following facts. ^1H resonance spectra in all samples appear as a broad resonance line at low temperatures, a narrow resonance line at high temperatures, and a superposition of a narrow component and a broad component at intermediate temperatures. The temperature dependence of linewidth of the narrow resonance line indicates the presence of mobile hydrogen.

^1H nuclear magnetization in CeNiAlH_x exhibits simultaneously two types of relaxation behavior at all hydrogen concentrations. In one type, which makes the dominant contribution to the total magnetization, the relaxa-

tion mechanism is dominated by localized magnetic moments, mainly through the Ruderman-Kittel-Kasuya-Yosida interaction, whereas the other type is characterized mainly by a Korringa mechanism. In CeCuAlH_x

also, there are at least two different components of the ^1H nuclear magnetization. However, the relaxation of both the components is influenced by the localized magnetic moments.

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