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1990 J. Phys.: Condens. Matter 2 1253

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^1H NMR study of ZrNiAlH_x and YNiAlH_x

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Received 24 May 1989, in final form 24 July 1989

Abstract. ^1H CW and pulsed NMR studies on the hydrides ZrNiAlH_x , with hydrogen concentration $x = 0.33$ and 0.53 , and YNiAlH_x , with hydrogen concentration $0.12 \leq x \leq 1.17$, have been performed in the temperature range 150–400 K. In the case of the Zr compounds, only a single resonance line has been observed; the linewidth remains almost unchanged over the whole temperature range studied. A superposition of two lines, one broad and one narrow, has been observed in the case of the Y compounds with $x \geq 0.75$ in the temperature range 220–320 K, whereas only a single line is observed for hydrides of YNiAl with $x \leq 0.66$ at all temperatures studied. The narrow component for the former and the single line for the latter exhibit similar features of motional narrowing due to hydrogen diffusion. Measurements of T_1 of the protons reveal that the relaxation process in YNiAlH_x at low temperatures (below 200 K) and in ZrNiAlH_x at all temperatures is dominated by interactions of ^1H nuclei with the unpaired conduction electrons at the Fermi level. In the high-temperature region, 200–400 K, T_1 for the narrow lines for the Y compounds at all hydrogen concentrations is characteristic of a diffusional dominated relaxation mechanism. Motion of hydrogen in the broad component is also revealed through relaxation measurements, although it is not clearly observed in the CW experiments. The pressure–composition isotherms, and the fact that below 200 K only a single T_1 is observed for the samples with $x > 0.75$, indicate that YNiAlH_x is a single-phase hydride. Hydrogen atoms occupy two types of interstitial sites in YNiAl , in which the mobility of hydrogen in one of the sites is higher than that in the other. The activation energies for these motions have been estimated to be 0.24 eV/atom and 0.33 eV/atom.

1. Introduction

The hydrogen absorption properties of intermetallic compounds of the type AXAl ($A = \text{Zr, Y, Th, U}$ etc and $X = \text{Ni, Cu}$ and Mn) have been studied recently [1, 2]. These compounds belong to the Fe_2P -type hexagonal crystal structure with the space group $\text{P}\bar{6}2\text{m}$ [3]. Jacob *et al* [2] measured the maximum hydrogen absorption capacities of ZrNiAl , YNiAl and UNiAl as 0.7 atom per formula unit, 1.5 atoms per formula unit and 2.5 atoms per formula unit, respectively. These hydrides also exhibit the Fe_2P -type structure, with almost the same lattice dimensions as before their hydrogenation except for $\text{ZrNiAlH}_{0.7}$, in which case the doubling of the c axis, as found in the original compound ZrNiAl , vanishes as a result of hydrogenation. The study [2] of the desorption isotherms of UNiAlH_x has indicated the existence of at least two hydride phases in this hydride at different hydrogen concentrations. The phase limits of UNiAlH_x coincide with the hydrogen capacities of ZrNiAl and YNiAl and this indicates the possibility of sequential filling of interstitial sites in these three intermetallic compounds.

Reports of ^1H nuclear magnetic resonance (NMR) measurements on these types of compound are available only for $\text{ThNiAlH}_{2.5}$ and $\text{UNiAlH}_{1.9}$ [4]. The superposition of a broad and a narrow ^1H NMR signal, observed in the case of the thorium compound in the temperature range 175–196 K, has been explained in terms of either the co-existence of two crystallographic phases or the hydrogen occupying two different crystallographic sites in the unit cell or a single-phase compound, in which the mobility of hydrogen in one of the sites of phases is higher than that in the other in the above temperature range. In the case of the hydride of UNiAl , an antiferromagnetic transition has been revealed through observation of the susceptibility maximum at 122 K and a simultaneous disappearance of the ^1H NMR signal.

In this paper, pressure–composition isotherms of YNiAlH_x and the results of ^1H NMR investigations on the hydrides of ZrNiAl and YNiAl are reported. Both continuous-wave (CW) and pulsed NMR measurements have been performed to study the diffusion of hydrogen in these hydrides.

2. Experimental details

The compounds ZrNiAl and YNiAl were prepared by arc-melting the constituent elements on a water-cooled copper hearth under an argon atmosphere. The process of melting was repeated several times to obtain a homogeneous compound. The samples were then annealed at 700 °C for more than 48 h. The crystal structures were confirmed by x-ray powder diffraction studies.

The hydrogenation of these compounds was carried out in a stainless steel reactor, the details of which have been discussed elsewhere [5]. This apparatus was modified for accurate pressure measurements by using Kistler piezoresistive pressure transducers. To activate the samples, they were initially hydrided at 200 °C, cooled to room temperature and then completely degassed for several hours at 500 °C to reach a vacuum of 10^{-2} torr. This process was repeated at least three times in each case. Final hydrogenations were performed under conditions of constant temperature and pressure except for the hydrides of ZrNiAl and the sample of concentration $x = 0.12$ in YNiAlH_x , in which case the experimental limitations prevented preparation of samples under equilibrium conditions at temperatures below 200 °C. The pressure against concentration isotherms were obtained by allowing a known amount of hydrogen gas to react with the sample during constant-pressure measurements. The hydrogen-to-metal ratio was calculated by the standard pressure–volume–temperature (P – V – T) method. The maximum error in the concentration (x) values was ± 0.05 . The prepared hydrides were stored in air without any further precautions. No loss of hydrogen was found during the NMR measurements, which were taken over several weeks.

All ^1H NMR data were taken by using either the CW method in field-sweep mode or the pulse method. The magnetic field was supplied by a field-dial regulated V7400 electromagnet. The CW absorption-derivative signals were taken in a Varian WL210 spectrometer at a resonance frequency of 15 MHz and in the temperature range 150–350 K. The temperature was varied by using a V4540 temperature controller. The actual temperature of the sample was independently measured by a chromel–alumel thermocouple.

The instrument used for pulsed NMR measurements was a Bruker MSL100 spectrometer combined with the same electromagnet. The absorption signal was obtained by Fourier transformation (FT) of the free-induction-decay (FID) signal observed after a

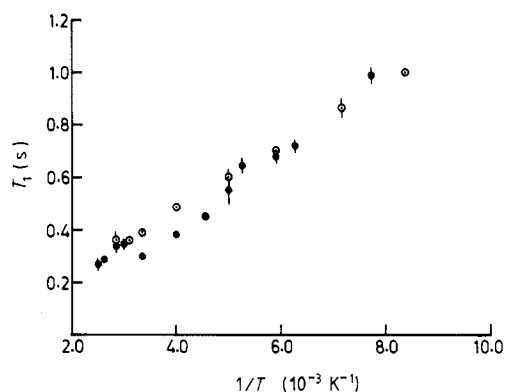


Figure 1. Plot of the ^1H spin-lattice relaxation time (T_1) against the inverse of temperature for $\text{ZrNiAlH}_{0.53}$ at resonance frequencies 34.0 MHz (●) and 95.0 MHz. (○).

$\sim 90^\circ$ pulse. The ^1H spin-lattice relaxation time (T_1) was measured in the temperature range 140–420 K mostly at 34 MHz using the inversion-recovery ($180^\circ\text{--}\tau\text{--}90^\circ$) technique. In the case of broad lines, the solid-echo sequence ($90^\circ\text{--}\tau\text{--}90^\circ$) was used as the monitoring pulse and thus the complete pulse sequence was $180^\circ\text{--}\tau\text{--}90^\circ\text{--}\tau_1\text{--}90^\circ_{(90^\circ)}\text{--}\tau_2\text{--}\text{echo}$. From the change in magnetisation with the delay time τ , obtained from the peak values of the Fourier-transformed signal taken at different τ values, the relaxation time (T_1) was determined.

During the T_1 measurements, the temperature of the sample was controlled to within $\pm 1^\circ\text{C}$ of the set temperature using a Bruker BVT1000 temperature controller. A copper-constantan thermocouple kept close to the sample monitored the temperature.

The magnetic susceptibility measurements were performed using a vibrating-sample magnetometer (VSM155 or EG&G) coupled to the same electromagnet. The V4540 temperature controller was used for temperature variation.

3. Results and discussion

3.1. ZrNiAlH_x

^1H NMR measurements on ZrNiAlH_x have been performed on samples having hydrogen concentrations $x = 0.33$ and 0.53 , the latter being the maximum concentration that has been achieved at a hydrogen pressure of 40 bar at 200°C . Both samples exhibit single resonance lines in the temperature range 150–400 K. In each of the samples, the width of the resonance line, measured as the peak-to-peak separation of the absorption derivatives, is ~ 4.0 Oe and remains almost unchanged in the entire range of temperature; also, it does not show any appreciable field dependence. The observation of a single resonance line throughout the temperature range indicates the system to be in a single phase at these hydrogen concentrations. The NMR results further indicate that only one type of site is available for hydrogen in the ZrNiAl lattice. It can also be said that any sort of diffusive motion of the absorbed hydrogen, if present below 400 K, is slow in comparison with the NMR frequency.

A study of the ^1H spin-lattice relaxation time (T_1) reveals that the magnetisation recovery follows a single exponential behaviour at any temperature in the range 140–420 K. The T_1 data (figure 1) follow the Korringa relation, $T_1 T = \text{constant}$. Thus, the

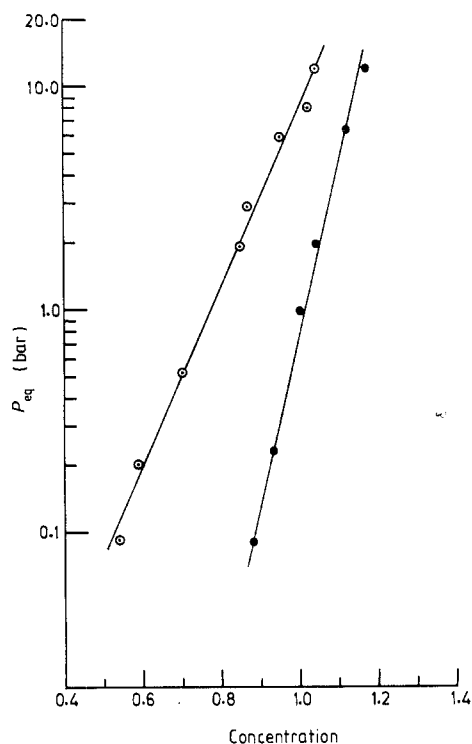


Figure 2. Pressure–composition (PC) absorption isotherms of the hydride of YNiAl at 400 K (●) and 500 K (○). The equilibrium hydrogen pressures (P_{eq}) have been plotted against hydrogen concentration in YNiAl.

relaxation process in this system is governed by interactions of ^1H nuclei with the magnetic field produced at the nuclear site by the unpaired conduction electrons at the Fermi level. The value of the Korringa product is ~ 110 s K, which is almost half of that which was found in $\text{ThNiAlH}_{2.5}$ [4]. The results suggest that the ZrNiAlH_x compounds are metallic.

3.2. YNiAlH_x

3.2.1. Pressure–composition (PC) isotherms. Figure 2 shows the PC absorption isotherms of the YNiAl–H system obtained at temperatures of 400 and 500 K. The equilibrium pressure is varied from 0.1 to 12.0 bar. None of these isotherms exhibits any plateau region. The PC characteristics reveal that, if there is a critical point below which there may be a co-existence of two phases, then this point must lie below the concentration $x \sim 0.8$ corresponding to the 400 K isotherm and this is to be obtained at a very low equilibrium pressure. However, as the two isotherms (figure 2) follow straight lines obeying Sievert's law, and, moreover, as their respective regions of concentration are seen to overlap to a large extent, it may be assumed that all the YNiAlH_x samples prepared under the above conditions belong to the same phase. Using Van't Hoff's relation, $\ln P_{\text{eq}} = -\Delta S/R + \Delta H/RT$, where P_{eq} is the equilibrium hydrogen pressure, the changes in enthalpy and entropy for $x = 0.9$ have been estimated as $\Delta H = -12.9$ kcal $(\text{mol H}_2)^{-1}$ and $\Delta S = -31.9$ cal $\text{K}^{-1} (\text{mol H}_2)^{-1}$, respectively. These values are nearly the same as those found in the isostructural systems ThNiAlH_x and UNiAlH_x [1, 2].

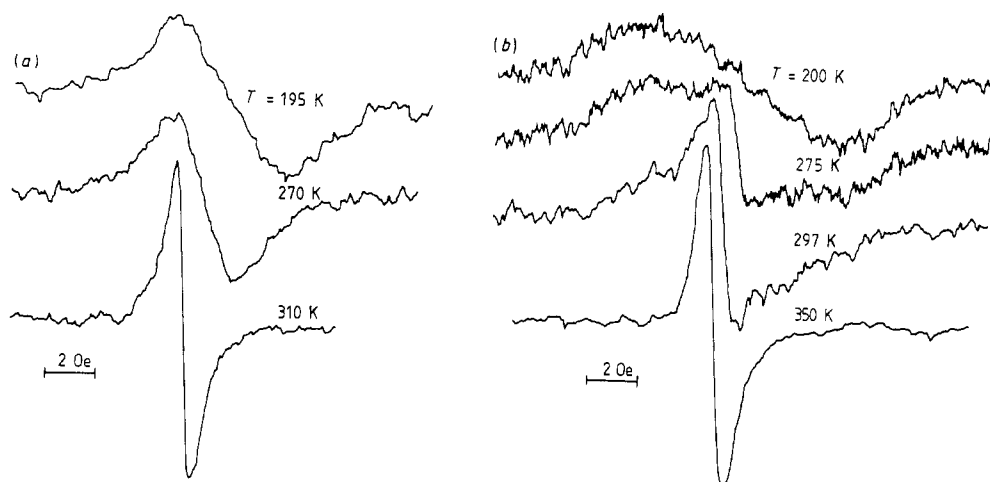


Figure 3. ^1H CW NMR spectra of YNiAlH_x at the resonance frequency 15.0 MHz for (a) $\text{YNiAlH}_{0.59}$ and (b) $\text{YNiAlH}_{1.17}$.

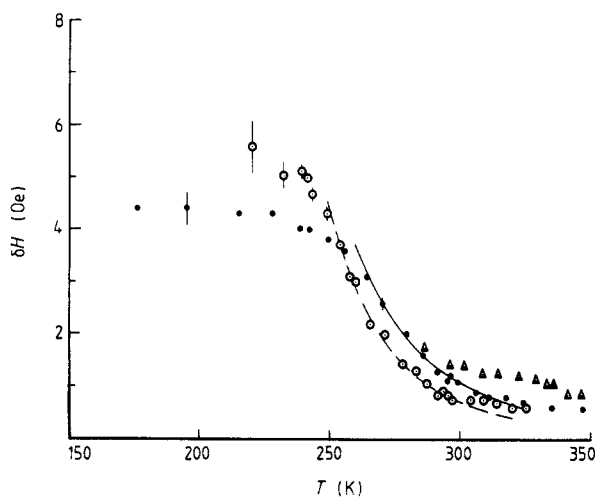


Figure 4. Temperature dependence of the linewidth (δH) of ^1H CW NMR lines at the resonance frequency 15.0 MHz: \bullet , $\text{YNiAlH}_{0.59}$; \circ , $\text{YNiAlH}_{1.0}$; \triangle , $\text{YNiAlH}_{1.17}$. The curves are theoretical fits to equation (4): —, $\text{YNiAlH}_{0.59}$; - - -, $\text{YNiAlH}_{1.0}$.

3.2.2. NMR results. The ^1H NMR measurements show that the samples with concentrations $x \leq 0.66$ exhibit a single resonance line in the entire range of temperature observed (figure 3(a)). The width of the resonance line (determined as the peak-to-peak separation of the absorption derivative) shows considerable temperature dependence in the temperature range 255–295 K. The linewidth increases as the temperature decreases until about 250 K, below which it becomes constant. The temperature dependence of the linewidth for $\text{YNiAlH}_{0.59}$ is shown in figure 4.

At higher hydrogen concentrations, $x \geq 0.75$, the room-temperature ^1H NMR spectra indicate a composite resonance line consisting of a narrow and a broad component. This feature is clearly observable in samples with $x \geq 1.0$, on which detailed cw experiments have been performed. Only a single broad line of linewidth ~ 8.0 Oe is observed at temperatures below 200 K. On increasing the temperature, a narrow component appears at around 220 K. The width of the narrow component decreases with increasing temperature. The broad component shows no remarkable change in its linewidth but, interestingly, its intensity is reduced with increasing temperature. Above 330 K the broad component is no longer observable and only a narrow line is obtained. Figure 3(b) shows the ^1H resonance spectra of $\text{YNiAlH}_{1.17}$ at different temperatures. The temperature dependence of the linewidth of the narrow component is shown in figure 4. Experiments with samples of lower hydrogen concentrations become difficult because of poor signal-to-noise ratios, especially at low temperatures. Also, at concentrations higher than $x \sim 1.0$, the broad component becomes stronger and the overlap of the two components at low temperatures makes it difficult to estimate the width of the narrow component.

The simultaneous appearance of two lines in YNiAlH_x for $x \sim 0.75$ and above could have been explained as a consequence of the co-existence of two crystallographic phases or the hydrogen atoms occupying two different sites in a single-phase hydride. However, as YNiAl does not undergo any structural change on hydrogenation [2] and, moreover, as the PC isotherms shown earlier indicate the hydrides to be in a single phase, it is more likely that the two lines are due to two types of sites being available for hydrogen in a single-phase compound. Only one of the sites, that corresponding to the narrow component, is preferentially occupied at lower concentrations.

To understand the behaviour of the narrow lines, the dependence of the linewidths on the magnetic field has been investigated. It is found that the linewidth (determined as the full-width-at-half-maximum) obtained from the FT spectra at 150 K for any hydrogen concentration remains constant over the frequency range 15–70 MHz. The linewidth in this case, therefore, is solely due to the nuclear dipolar field and the bulk magnetic susceptibility does not contribute. Obviously, the main source of linewidth would be from proton dipole–dipole interaction. But there are other nuclei, namely ^{27}Al and ^{89}Y , which possess nuclear dipole moments, and interactions among the dissimilar nuclei, i.e. ^1H – ^{27}Al and ^1H – ^{89}Y , make small contributions to the total linewidth. Furthermore, measurements of the magnetic susceptibility in the range 150–300 K reveal that YNiAl as well as its hydrides are Pauli paramagnetic, i.e. they exhibit temperature-independent magnetic susceptibility at all hydrogen concentrations. Thus the temperature dependence of the linewidth of the narrow lines, as observed here, is not due to magnetic broadening by the presence of magnetic impurities. Instead, it can be understood in terms of a diffusion process of the hydrogen atoms which, when considered, allows a large portion of the nuclear dipole–dipole interaction to be averaged out by the motion of protons with a consequent narrowing of the observed linewidth.

The temperature dependence of the correlation time for the proton magnetic dipole interaction is found by fitting the linewidth (δH) against temperature plots to the theory of Kubo and Tomita [6]. 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

$$(1/T_2')^2 = (4 \ln 2/\pi) \langle \Delta\omega^2 \rangle \tan^{-1} [\pi\tau_c / (4 \ln 2) T_2'] \quad (1)$$

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

Table 1. Korringa product (T_1T), activation energy (E_a) for hydrogen motion and pre-exponential factor (ν_0) for YNiAlH_x at different hydrogen concentrations (x).

x	T_1T (s K)	E_a^a (eV/atom)	E_a^b (eV/atom)	ν_0 (Hz)
0.12	200	0.25 ± 0.01	—	—
0.59	200	0.26 ± 0.01	0.21 ± 0.03	$(4.2 \pm 1.0) \times 10^8$
1.0	77	0.23 ± 0.01^c	0.23 ± 0.01	$(3.3 \pm 1.0) \times 10^9$
1.17	97	0.26 ± 0.01^c 0.33 ± 0.01^d	—	—

^a Derived from the temperature dependence of the ^1H spin–lattice relaxation time (T_1).

^b Derived from the temperature-dependence of the ^1H resonance linewidth.

^c For the narrow component, as defined in the text.

^d For the broad component.

$$(1/\tau_c) = \nu_c = \nu_0 \exp(-E_a/kT) \quad (2)$$

where E_a is the activation energy required for the motion of protons, ν_c is the correlation frequency and ν_0 the pre-exponential factor. Small uncertainties in E_a produce large uncertainties in ν_0 and any more precise definition and consideration of ν_0 than given above is not appropriate for this experiment because of the uncertainties in E_a . At high temperatures, where $\tau_c \ll T_2'$, equation (1) becomes

$$1/T_2' \approx \langle \Delta\omega^2 \rangle \tau_c \approx (\langle \Delta\omega^2 \rangle / \nu_0) \exp(E_a/kT). \quad (3)$$

Now, for a Lorentzian line, $1/T_2' = (\sqrt{3}/2)\gamma(\delta H)$ and, since the rigid-lattice line-shape is Gaussian, $\langle \Delta\omega^2 \rangle$ can be replaced by $(\gamma\delta H_0)^2/4$ where δH_0 is the peak-to-peak separation of the absorption derivative of the rigid-lattice resonance line. Equation (3) can therefore be expressed as

$$\delta H = [\gamma(\delta H_0)^2/2\sqrt{3}]\nu_0^{-1} \exp(E_a/kT). \quad (4)$$

Equation (4) is fitted to the observed δH for each concentration (x) of hydrogen and the values of E_a and ν_0 determined are listed in table 1. To understand the detailed nature of the motion, ^1H spin–lattice relaxation studies have been performed.

Measurements of the ^1H spin–lattice relaxation time (T_1) in the temperature range 140–400 K have been performed in YNiAlH_x at various hydrogen concentrations between $0.12 \leq x \leq 1.17$. From the experimental results, the samples can be divided into two groups. In the first group, in which the hydrogen concentration is in the range $0.12 \leq x \leq 0.66$, the samples exhibit a single T_1 at any temperature. The temperature dependence of T_1 shows no significant variation with hydrogen concentration. On the other hand, for the samples belonging to the second group, with hydrogen concentration $0.75 \leq x \leq 1.17$, the change in magnetisation ($M_0 - M$) with the delay time τ does not follow a single exponential behaviour at temperatures above 200 K. However, this is not surprising as the CW NMR spectra mentioned earlier reveal the existence of two types of protons, one of which shows considerable mobility. In this case, therefore, there is a possibility of finding at least two different relaxation times (T_1). The plots of $\ln(M_0 - M)$ against τ at any temperature above 200 K exhibit two linear regions corresponding to two different values of T_1 , namely T_{1a} and T_{1b} , of which $T_{1a} < T_{1b}$. We assign T_{1a} for the narrow component and T_{1b} for the broad component of the CW spectra (figure 3(b)). At

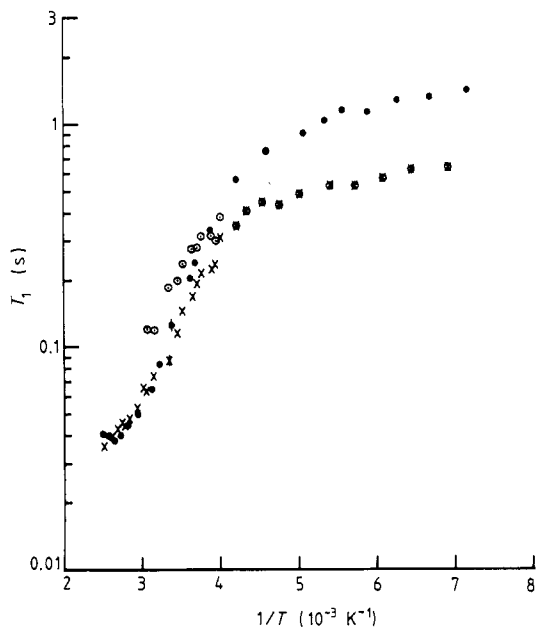


Figure 5. Plot of the ^1H spin-lattice relaxation time (T_1) against the inverse of temperature at the resonance frequency 34.0 MHz: ●, $\text{YNiAlH}_{0.59}$; ×, T_{1a} in $\text{YNiAlH}_{1.17}$; ○, T_{1b} in $\text{YNiAlH}_{1.17}$; ⊗, $T_{1a} = T_{1b}$. T_{1a} and T_{1b} are defined in the text.

temperatures above 320 K the contributions due to the broad component in the spectra become very small (as evident from the cw spectra) and as such the estimation of T_{1b} becomes less accurate.

The temperature dependence of T_1 for $\text{YNiAlH}_{0.59}$ and that of T_{1a} and T_{1b} for $\text{YNiAlH}_{1.17}$ are shown in figure 5. In general, the observed relaxation rate (T_1^{-1}) consists of several independent contributions:

$$T_1^{-1} = T_{1d}^{-1} + T_{1e}^{-1} + T_{1p}^{-1} \quad (5)$$

where T_{1d} is due to the modulation of the proton dipolar interactions because of atomic diffusion, T_{1e} represents the relaxation processes from interactions with the unpaired conduction electrons at the Fermi level and T_{1p} describes the interactions with the paramagnetic atoms (i.e. localised magnetic moments). The last term, in the present case, can be neglected as the samples have been found to be Pauli paramagnetic. Starting at 400 K, the rapidly rising portion of T_1 (figure 5) in all cases is characteristic of a diffusively dominated relaxation mechanism. The flattening-out portion of the T_1 curve at lower temperatures reveals the growing importance of the conduction-electron contribution. Therefore, at low temperatures, where the diffusional contribution is negligible, $T_1^{-1} \approx T_{1e}^{-1}$. Indeed, at temperatures below 200 K the observed relaxation time has been found to follow the Korringa relation $T_1 T = \text{constant}$, suggesting that all these hydrides are metallic. The values of the Korringa product (table 1) are considerably smaller at high hydrogen concentrations than those for samples with lower hydrogen concentrations. This probably indicates that the electronic density of states at the Fermi level becomes higher at high hydrogen concentrations in the YNiAlH_x system.

The diffusional contribution (T_{1d}^{-1}) at any temperature can be separated out from equation (5) by subtracting T_{1e}^{-1} , the values of which at high temperatures are obtained by extrapolating the linear plot of T_1 against $1/T$ for low temperatures. The simplest (BPP)

model for describing the diffusionally dominated relaxation time relates the correlation time of the diffusing nucleus to the observed value of T_1 assuming that the dipolar field correlations decay as $\exp(-t/\tau_c)$. More accurate models which attempt to account for the orientation-dependent jumps between the specific lattice sites in solids were later developed [7, 8]. However, the complexities of the resulting numerical analysis have limited their applications to the few high-symmetry cubic structures. Furthermore, these lattice-specific models usually exhibit the same qualitative behaviour as the simple BPP model [7, 9].

According to the BPP model, T_{1d}^{-1} for the H-H dipole interaction that is modulated by the motion of the H atoms is given by

$$T_{1d}^{-1} = C[\tau_c/(1 + \omega^2\tau_c^2) + 4\tau_c/(1 + 4\omega^2\tau_c^2)]$$

where τ_c is the correlation time, ω is the angular resonance frequency and C is a constant independent of ω and τ_c . This equation predicts a minimum of T_1 near $\omega\tau_c = 0.62$. Some curvature of T_1 at high temperatures can be seen in figure 5. Experimental limitations prohibit us from searching for a minimum at higher temperatures. In the temperature region, $\omega\tau_c \gg 1$, when τ_c fits the Arrhenius relation $\tau_c = \tau_0 \exp(E_a/kT)$, T_{1d} can be written as $T_{1d} = C' \exp(E_a/kT)$; where C' is a constant. Thus a linear plot of $\ln T_1$ as a function of reciprocal temperature provides an estimate of the activation energy (E_a) for hydrogen diffusion. Table 1 gives the values of E_a for samples of different hydrogen concentrations.

It may be seen (table 1) that the values of E_a for protons corresponding to the narrow lines are nearly the same for all hydrogen concentrations. For $x = 1.17$, in which both components, the narrow and the broad, have significant contributions in the spectra, T_1 measurements show that not only the narrow component but also protons belonging to the broad component both exhibit some sort of motion as observed in the temperature dependence of T_{1b} in the region 250–320 K (figure 5). The activation energy corresponding to this motion is slightly higher than that observed in the narrow component. It may be pointed out that this motion in the broad component has not been clearly revealed from the linewidth in the cw experiments (figure 3(b)). The temperature dependence of T_{1b} combined with the behaviour of the broad component (figure 3(b)) with temperature indicates that the increase of temperature facilitates the exchange of hydrogen atoms between the two types of sites and that, at high temperatures, all the sites become equivalent as far as the motion of hydrogen is concerned. It is reasonable to suppose that the separations of like and unlike sites are similar. At intermediate temperatures, the effect of higher hydrogen mobility in one of the sites, corresponding to the narrow component, should have been manifested in the linewidth of the broad component because of significant dipolar couplings between unlike sites, as should be the case if the compound is in a single phase. In the present case, however, any change in the linewidth of the broad component could not be observed as its intensity is drastically reduced as the temperature increases (figure 3(b)). The motional behaviour of T_{1b} could, however, be ascribed to the cross-coupling as stated above. But that alone cannot explain the observed spectral behaviour, i.e. the disappearance of the broad component at high temperatures. Furthermore, at low temperatures, T_{1a} and T_{1b} are determined solely by the electronic contribution as mentioned earlier, and presumably their equality reflects the common electronic structure of the two types of site in a single-phase compound.

4. Conclusion

^1H NMR measurements in ZrNiAlH_x with hydrogen concentration $x = 0.33$ and 0.53 and in YNiAlH_x with $0.12 \leq x \leq 1.17$ reveal the following facts. In the case of the Zr compounds, only a single resonance line corresponding to a single hydrogen site arises without showing any substantial hydrogen mobility in the lattice. A single line is also observed in YNiAlH_x with $x \leq 0.66$; in this case, however, motional narrowing is observed due to diffusion of hydrogen with an activation energy of about 0.24 eV. A superposition of two lines is observed in the same system with $x \geq 0.75$. The narrow component shows the same feature of hydrogen diffusion as stated above. Relaxation studies reveal features of the hydrogen mobility even for the broad component with an activation energy of 0.33 eV. From the PC isotherms, and the fact that only one relaxation time is obtained at low temperatures (below 200 K) for the hydrides of YNiAl with $x \geq 0.75$, we can conclude that all these hydrides belong to the same single-phase compounds. Thus the hydrogen atoms occupy two types of interstices in the unit cell in which the mobility of hydrogen in one of the sites is higher than that in the other. In the absence of detailed structural information of the hydride system, the site occupancy of the hydrogen atoms could not be calculated from the linewidth of the ^1H NMR line in the rigid-lattice state.

Acknowledgment

We are grateful to Dr K Roychowdhuri of the Geological Survey of India, Calcutta, for carrying out the x-ray powder diffraction studies of the prepared samples.

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