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^1H NMR and magnetic susceptibility study of $ThNiAlH_x$ and $UNiAlH_x$

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A continuous-wave (cw) and pulsed-proton nuclear-magnetic-resonance (NMR) study was conducted on two Fe_2P-type compounds, $ThNiAlH_x$ and $UNiAlH_x$, where $x = 2.5$ and 1.9 for the thorium and uranium compounds, respectively. The proton cw NMR spectra of the $ThNiAlH_x$ compound show a broad line (~ 9 Oe) below 175 K, a narrow line (~ 1 Oe) above 196 K, and a superposition of a broad and a narrow line between these two temperatures. The simultaneous appearance of two lines may be explained in terms of either the coexistence of two crystallographic phases or the hydrogens occupying two different crystallographic sites of a single-phase compound in which the mobility of the hydrogen in one of the phases, or sites, is higher than that in the other phase above 175 K. The activation energy for hydrogen diffusion in $ThNiAlH_x$ was deduced from the spin-lattice relaxation time T_1 to be 11 kJ/mole based on the Bloembergen, Purcell, and Pound model. Spin-lattice relaxation time T_1 and the magnetic-susceptibility results indicate the existence of two antiferromagnetic transition temperatures, one at 122 K and the other at 34 K, in $UNiAlH_x$. It is most likely that the $UNiAlH_x$ contains two antiferromagnetic phases with $T_N = 122$ and 34 K.

I. INTRODUCTION

In contrast to binary metal hydrides, the magnetic and structural properties of intermetallic hydrides are relatively little known even though their ability to absorb and desorb hydrogen is important to their technical application.[1,2] Also of importance to technical application of intermetallic hydrides is the role of hydrogen in greatly modifying the magnetic properties of these compounds. For instance, Y_6Mn_{23}, a ferromagnet, behaves as a paramagnet[3] after it absorbs hydrogen. In contrast, Th_6Mn_{23} is a paramagnet, but after hydrogenation it exhibits ferromagnetic ordering.[3] The ThNiAl and UNiAl compounds have the Fe_2P-type hexagonal structure[4] shown in Fig. 1. Under high pressure they are able to absorb hydrogen with a H/ThNiAl ratio equal to 3 and a H/UNiAl ratio equal to 2.3. The crystallographic data indicate that, at room temperature, the type of structure after hydrogenation remains the same as the pure compound, although the volume of the unit cell increases by about 10%.

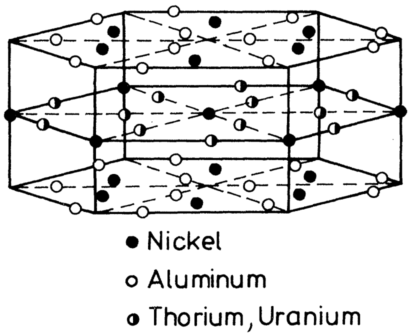

FIG. 1. Atomic arrangement in Th/UNiAl. This is the hexagonal Fe_2P-type structure, space group $P\bar{6}2m$.

In this paper, we report proton nuclear-magnetic-resonance (NMR) results on $ThNiAlH_x$ and $UNiAlH_x$ and magnetic susceptibility measurements on UNiAl and $UNiAlH_x$.

II. EXPERIMENTAL

Sample preparation is described in a separate paper.[5] The H/ThNiAl and H/UNiAl ratios, as determined by measuring the amount of absorbed hydrogen at high pressure (3.9 MPa) and room temperature, were 3 and 2.3, respectively. Samples for NMR measurements were encapsulated in a glass tube under an argon atmosphere in a glove box. During the encapsulation process we were not able to maintain the concentration-pressure equilibrium condition and thus some hydrogen was released from the samples. Therefore, after NMR measurements, we analyzed the hydrogen concentration in the samples by thermal decomposition in an appropriate vacuum apparatus. The values of $x=1.9$ and 2.5 were found for UNiAlH$_x$ and ThNiAlH$_x$, respectively. Magnetic susceptibility measurements were made using the Faraday method and the data were recorded continuously in a magnetic field of 0.4 T in a temperature range 4.2—300 K.

All continuous-wave (cw) NMR data were taken with a Varian wide-line nuclear induction spectrometer. Nuclear magnetic resonance of ^{1}H was observed at 35 MHz and temperatures between 78 and 300 K. Pulsed NMR measurements were made with a phase-coherent and pulse-coherent spectrometer employing phase-sensitive detection and a Nicolet Instruments signal averager. The measurements were made between 78 and 300 K at a frequency of 12 MHz. The magnetic field was supplied by a Varian electromagnet with Fieldial control. Measurements of spin-lattice relaxation times T_1 were made by using either $\frac{1}{2}\pi-\tau-\frac{1}{2}\pi$ or $\pi-\tau-\frac{1}{2}\pi$ pulse sequence. Longitudinal relaxation curves were observed until τ equaled (1.1—2) T_1, and were exponential.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. ThNiAlH$_x$

Proton cw NMR spectra obtained at low temperature consist of one broad line. The linewidth, determined as the distance between the derivative maxima of the absorption curve, is equal to (8.8±0.4) Oe with the second moment equal to (9±1) Oe^2 at 78 K. When the temperature is increased to 168 K no appreciable change in the shape of the resonance line is observed. However, at 175 K the spectrum is a superposition of a broad and a narrow line. The linewidth of the former is the same as that observed at 78 K, while the narrow component is about 1 Oe wide. Further increase of temperature enhances the narrow line at the expense of the broad component. This behavior is shown in Fig. 2. At room temperature only a single line, 0.7 Oe wide, is observed. One possible explanation of these data is that at low temperatures the hydrogen atoms occupy fixed positions in the crystal lattice. Accordingly, a proton dipole-dipole interaction would be the main source of linewidth observed, and the width of the resonance would be several Oe. The second moment of the resonance line, often used to withdraw structural information, should, in this case, depend on the particular position of protons in the unit cell. Unfortunately, the lack of any low-temperature structural information on ThNiAlH$_x$ prevents comparing the experimental value of the second moment with theory. The narrow NMR spectral component observed at higher temperatures is difficult to explain in terms of a rigid lattice. Instead, it can be understood in terms of the diffusion process of hydrogen atoms which, when considered, allows a large portion of the dipole-dipole interaction to be averaged out by motion of the protons with a consequent narrowing of the observed linewidth. The simultaneous appearance of two lines may be explained as a consequence of the coexistence of two crystallographic phases or the existence of two different hydrogen sites in the unit cell of a single-phase compound. In either case, the hydrogen mobility is the factor controlling the two signals. Double spectra such as these were also observed by Hon[6] for the zirconium hy-

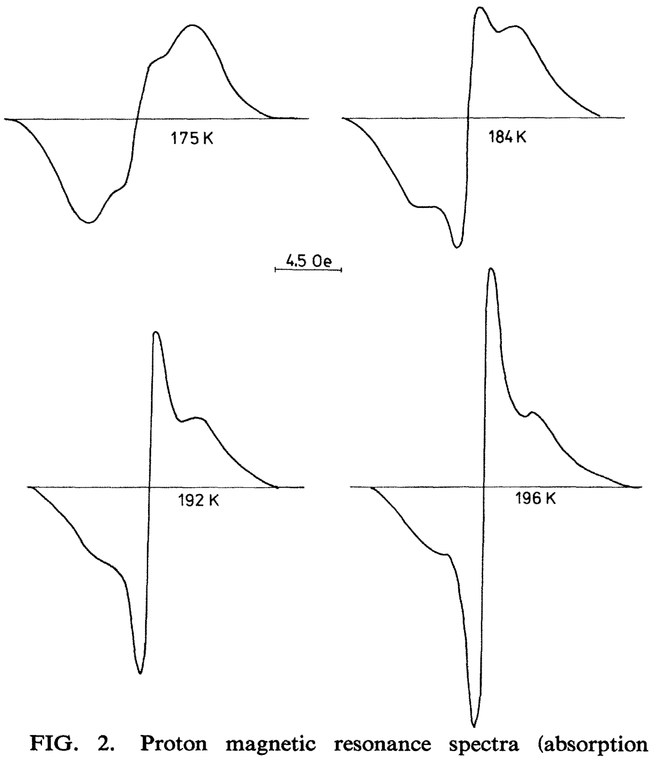

FIG. 2. Proton magnetic resonance spectra (absorption derivatives) in ThNiAlH$_x$ at temperatures 175—196 K, showing superposition of a broad and a narrow resonance line.

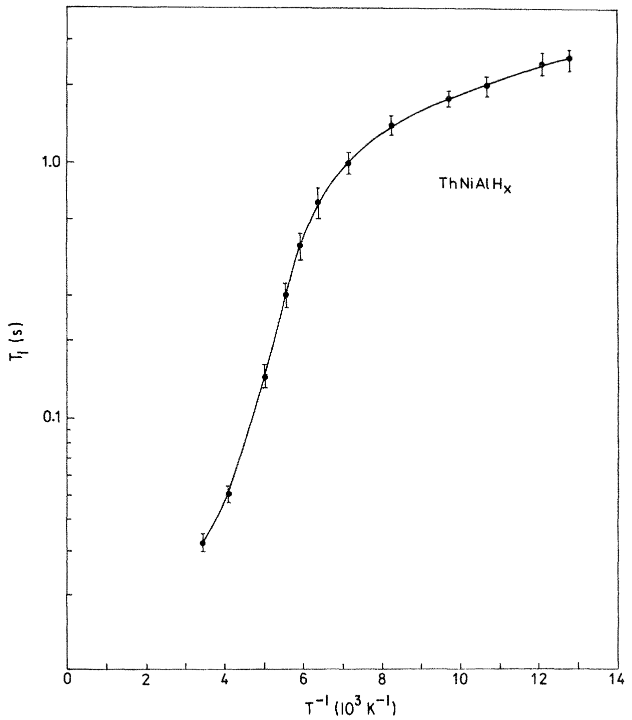

FIG. 3. Dependence of the proton spin-lattice relaxation time T_1 on inverse temperature in ThNiAlH$_x$.

drides and by Weaver[7] for the YH_x system. Hon argued that the superimposed resonance lines were the result of hydrogen moving along different paths between interstitial sites of the same type. On the other hand, Weaver suggested that sample inhomogeneity probably accounts for the double spectra in yttrium hydride with high hydrogen concentration.

The temperature dependence of the spin-lattice relaxation times T_1 for $ThNiAlH_x$ is shown in Fig. 3. Starting at room temperature, T_1 increases rapidly with decreasing temperature until about 161 K, below which T_1 increases much less rapidly. In the rapidly rising portion of the curve in Fig. 3 we assume that the dominant contribution to T_1 is the diffusion of protons. Bloembergen *et al.*[8] developed a model which combines the correlation time of a diffusing NMR nucleus with the observed values of T_1. Although their model was later modified,[9–12] it is still widely used because of its simplicity and practicality. Moreover, no significant difference in the activation energy for proton diffusion was found between the model of Bloembergen *et al.* and the Torrey theory[9] with respect to titanium hydride.[13] According to the model of Bloembergen *et al.*, T_1^{-1} for H-H dipole interaction that is modulated by random jumps of H atoms is given by

$$T_1^{-1}=C\left[\frac{\tau_c}{1+\omega^2\tau_c^2}+\frac{4\tau_c}{1+4\omega^2\tau_c^2}\right], \tag{1}$$

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 in T_1 near $\omega\tau_c \simeq 1$. Some curvature of T_1 at room temperature can be seen in Fig. 3. However, the sample easily loses hydrogen above room temperature and this precludes measurements of T_1 at higher temperature. In the temperature range $\omega\tau_c \gg 1$, when τ_c fits the Arrhenius relation $\tau_c=\tau_0\exp(E_a/RT)$, the T_1 can be written as

$$T_1=c'\exp(E_a/RT), \tag{2}$$

where c' is a constant, E_a is the activation energy, R is the universal gas constant, and T is the temperature.

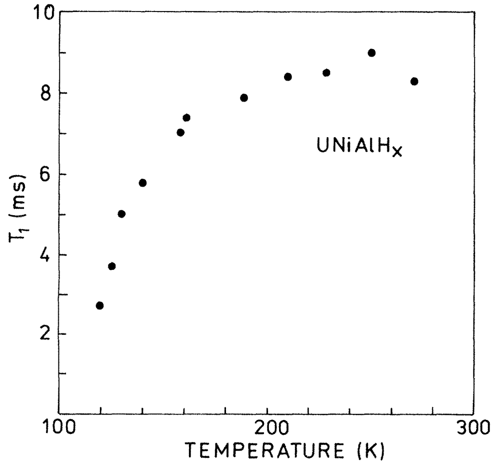

FIG. 4. Temperature dependence of the proton spin-lattice relaxation time T_1 in $UNiAlH_x$.

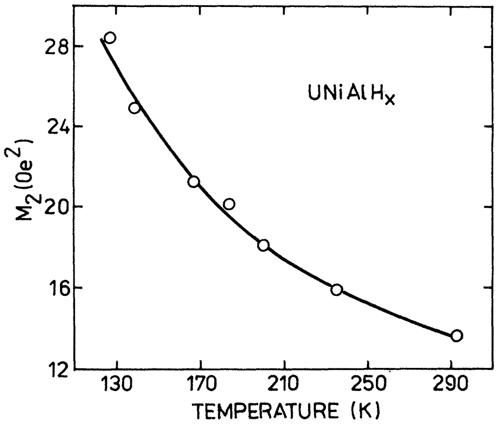

FIG. 5. Temperature dependence of the proton resonance second moment in $UNiAlH_x$ measured at a nominal frequency of 35 MHz. Solid line is least-squares fit of the data to Eq. (3), with $M_2(0)=7.8$ Oe^2.

Thus, a linear plot of $\ln T_1$ as a function of reciprocal temperature provides an estimate of the activation energy for hydrogen diffusion. Using this procedure, we obtained $E_a=11$ kJ/mol. Strictly speaking, for $ThNiAlH_x$, Eq. (1) should contain an additional term to account for the dipolar interaction between ^{1}H and ^{27}Al (the contribution of ^{61}Ni can be neglected because it is present in only small amounts and it has a small gyromagnetic factor, and also because the Th nucleus has no magnetic moment). However, Eq. (2) remains valid even when this term is included, as long as $\omega\tau_c \gg 1$.

The T_1 data for the low-temperature region follow a Korringa[14] relation with the product $T_1T=200$ sK. This suggests that the "low-temperature" phase is metallic, but the relatively high value of the Korringa product

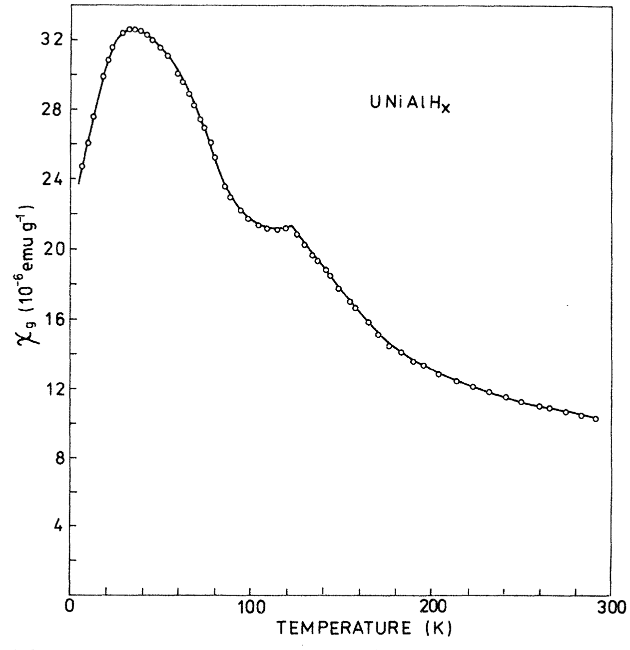

FIG. 6. Temperature dependence of the magnetic susceptibility in $UNiAlH_x$. The anomalies near 34 and 122 K are visible.

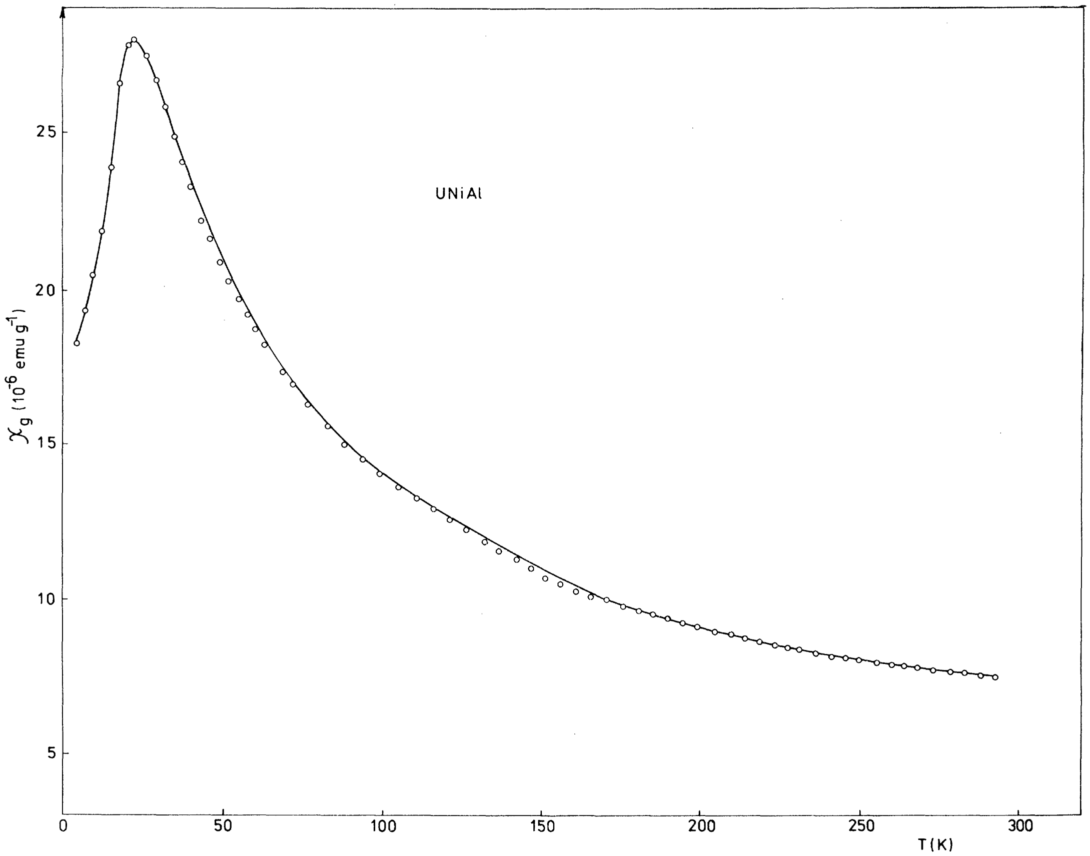

FIG. 7. Temperature dependence of the magnetic susceptibility in UNiAl with a pronounced maximum at 23 K.

indicates that the electron density of states at the proton site is low. It should be noted that the hydrides with high electron density of states, such as VH_2 (Ref. 15) and TiH_2,[16] have T_1T values between 30 and 60 s K.[17,18]

B. UNiAlH$_x$

The plot of spin-lattice relaxation time versus temperature is shown in Fig. 4. Note the much smaller absolute values of T_1 (as compared with ThNiAlH$_x$) and the lack of data below 120 K. The proton cw NMR spectra are generally asymmetric in shape, and for their characterization the second-moment value (with respect to the center of gravity) was used rather than the linewidth. The temperature dependence of the second moment is shown in Fig. 5. The second moment increases with decreasing temperature up to 128 K and only a narrow [(1—2)-Oe] resonance line of very low intensity can be seen at 77 K and 87 K. This behavior strongly suggests magnetic ordering below 128 K. To check this possibility, we measured the magnetic susceptibility of this sample. The results are shown in Fig. 6. We observed susceptibility maxima at 34 and 122 K. The maximum at 122 K coincides with the disappearance of the NMR signal. A maximum at 23 K has also been observed in the magnetic susceptibility data on UNiAl (Fig. 7). It is possible that the UNiAlH$_x$ sample contains two phases, one with a magnetic susceptibility maximum at 34 K and the other with a magnetic ordering temperature at 122 K. The former may probably be a hydrogen solid solution of UNiAl while the latter may be a hydride phase. The hydrogen dissolved in UNiAl would be responsible for shifting and broadening the susceptibility maximum of UNiAl from 23 to 34 K in UniAlH$_x$. The magnetic susceptibility maximum and the disappearance of the NMR signal sug-

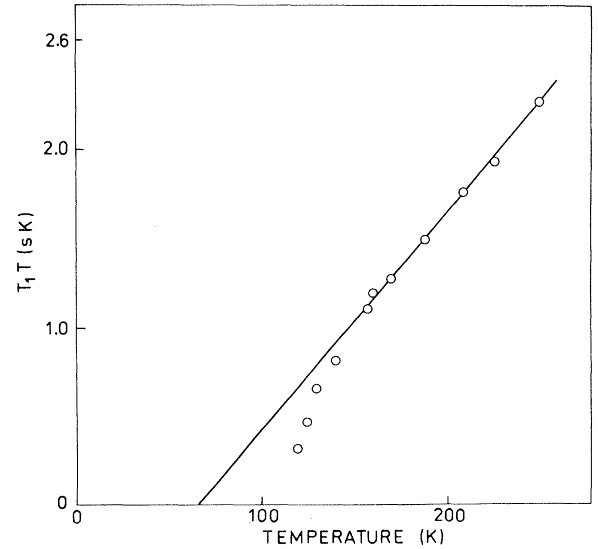

FIG. 8. Absolute-temperature product T_1T vs temperature T for proton NMR in UNiAlH$_x$.

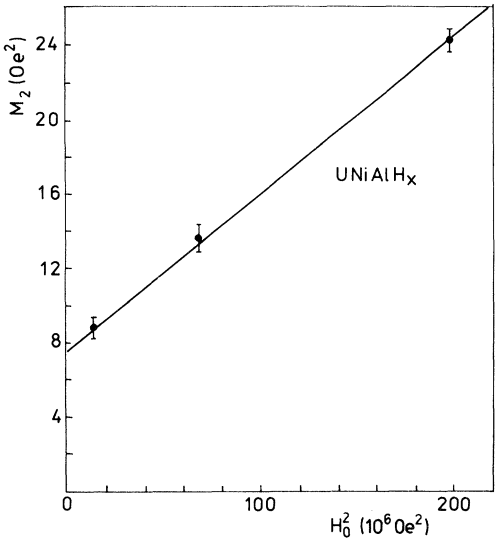

FIG. 9. Second moment of proton NMR line for UNiAlH$_x$ as a function of square of magnetic field (H_0^2). The measurements were made at room temperature. Straight line is least-squares fit of the data to the linear dependence of M_2 on H_0^2.

gests magnetic ordering at 122 K for the hydride phase.

The temperature dependence of the product of spin-lattice relaxation time and the absolute temperature, T_1T, for a nonactinide nucleus in local-moment systems, characteristically follows a linear temperature dependence for $T \gtrsim 1.3T_c$. This behavior of T_1T has been found in phosphides of uranium[19] and plutonium[20] as well as in hydrides of uranium[21] and plutonium.[22] In Fig. 8 we present a plot of T_1T versus temperature for UNiAlH$_x$. The values of $d(T_1T)/dT = 12$ ms and $\Theta = 64$ K are obtained from the linear part of the plot of T_1T versus temperature. The value of $d(T_1T)/dT$ for ferromagnetic uranium hydride[21] is close to what was found for UNiAlH$_x$. The value of $\Theta(Q)$, obtained from the intercept at which T_1T crosses the T axis, depends on the wave-vector-dependent susceptibility $\chi^{\pm}(q)$ where wave vector q is equal to Q and is maximized.[23] For antiferromagnets, $\chi^{\pm}(q)$ peaks away from $q=0$ and there is no correspondence between the Curie-Weiss temperature and $\Theta(Q)$. It is interesting to note that NpP, which is antiferromagnetically ordered below 120 K,[24] has $\Theta(Q) = 61$ K, which is quite close to the value observed in our sample.

The second moment M_2 of the proton cw NMR spectrum, as shown in Figs. 5 and 9, is both temperature and field dependent. This dependency is expected for paramagnetic materials[25] in which the M_2 is proportional to the square of magnetization. The results of plotting the measured M_2 as a function of H_0^2 at room temperature are shown in Fig. 9. The linear plot yields $M_2(0) = 7.8$ Oe^2 and the slope equals 8.3×10^{-8}. The data presented in Fig. 5 fit very well with the relation

$$M_2 = M_2(0) + \frac{C_m}{(T+\Theta)^2} , \tag{3}$$

with $\Theta = 66$ K and $C_m = 7.4 \times 10^5$ (Oe K)^2 when $M_2(0) = 7.8$ Oe^2 is used. The $M_2(0)$ can be compared with that calculated if the positions of the hydrogen atoms in the crystal lattice are known. Therefore, investigation of the crystal structure of this compound by neutron diffraction would be most useful.

Finally, we note that the measured proton Knight shift referred to the center of gravity of the NMR spectrum is equal to $(+0.015 \pm 0.01)$ % and does not show temperature dependence within experimental error. This result should be viewed with some caution since the NMR spectrum is asymmetrical in shape, possibly a result of superposition of two resonance lines.

IV. CONCLUSIONS

The main finding concerning UNiAlH$_x$ arises from proton-localized magnetic moment interaction. Both NMR and magnetic susceptibility data indicate antiferromagnetic ordering below 122 K. The second maximum in the magnetic susceptibility at 34 K is interpreted to indicate the antiferromagnetic transition temperature of a solid solution of UNiAl and hydrogen. In ThNiAlH$_x$, the proton spin-lattice relaxation rates are dominated by proton-diffusion and hyperfine-interaction contributions. Two resonance lines were clearly visible in the temperature range 175—216 K. Additional structural studies are needed to determine whether these lines are caused by the presence of two phases or two different proton environments in a single-phase compound. However, in view of the UNiAlH$_x$ results, it is proposed that this compound also contains two phases; a hydride and a solid-solution phase.

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