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## LETTER TO THE EDITOR

### Low-temperature $^1\text{H}$ NMR spectra of $\text{AlH}_3$

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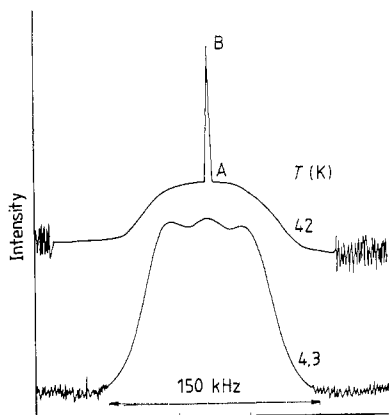
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**Abstract.** We report proton nuclear magnetic resonance measurements on aluminium trihydride over the temperature range 4.3–300 K. The spectra consist of two resonance lines with different widths. While the broad resonance is specific for  $\text{AlH}_3$  bulk material, the second one exhibits characteristics typical of molecular hydrogen surface coverage. The line broadening for this line has been observed between 10 K and about 4.6 K and the activation energy of 0.17 kcal mol<sup>-1</sup> for the self-diffusion process has been determined. The second and fourth moments for the lowest temperature range are close to those of HCP solid hydrogen (75% ortho-hydrogen concentration). The above data are consistent with an assumption that the second component of the spectra originates from thin (probably monolayer) molecular hydrogen surface coverage.

The proton absorption spectra presented in this letter represent an extension of CW NMR data previously reported [1] for the same sample. The characteristic feature of the earlier results was the presence of two lines in the spectrum over the entire measured temperature range, i.e. 300–78 K. One of these lines with a linewidth of about 17 Oe has been described as specific for bulk  $\text{AlH}_3$  hydride. No definite statement concerning the other narrow and low-intensity line has been made. There was a suggestion that it could be due to hydrogen molecules adsorbed on the surface. Very fast molecular motion would be responsible for the narrow and practically constant linewidth. Therefore it is expected that experiments at still lower temperatures, down to liquid helium temperature, should give additional arguments in favour (or against) the tentative interpretation mentioned above.

It is worth pointing out that the narrow component in the proton NMR of hydrides has been observed by a number of scientists [2–5]. These reports proposed either no explanation at all or only a few explanations for this phenomenon. In the case of  $\text{LaNi}_5\text{H}_x$  [4], for example, the authors concluded that the narrow resonance line is the result of a surface coverage by molecular hydrogen. However, they were not able to observe this component below  $\sim 10$  K, probably because of the high magnetic susceptibility of the material.

Here we would like to report  $^1\text{H}$  NMR data obtained in the 300–4.3 K temperature range using a Bruker MSL-300 pulse spectrometer at a frequency of 42.4 MHz. The spectra were obtained by Fourier transformation of the free induction decay (FID) following a 90° (3.8  $\mu\text{s}$ ) pulse. The sample temperature was controlled by methods and associated instrumentation described elsewhere [6].

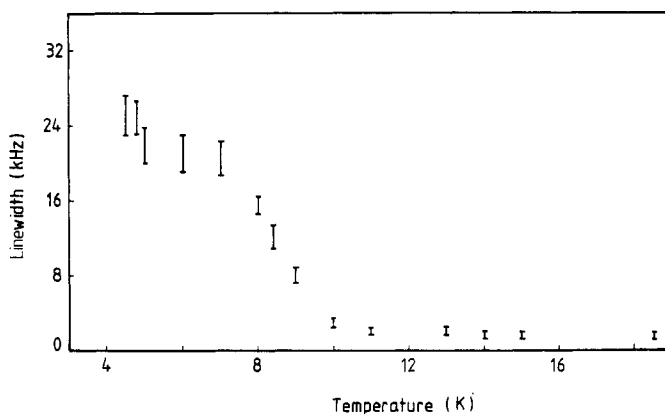


**Figure 1.** Recorded  $^1\text{H}$  NMR absorption spectra of  $\text{AlH}_3$  at  $T = 42$  K and  $T = 4.3$  K. The following settings were used: spectral width, 250 kHz; receiver bandwidth, 2 MHz; repetition time, 180 s ( $T = 4.3$  K) and 30 s ( $T = 42$  K); the number of transients were 18 and 60 for top and bottom traces, respectively. The noise level is marked on both edges of the spectra.

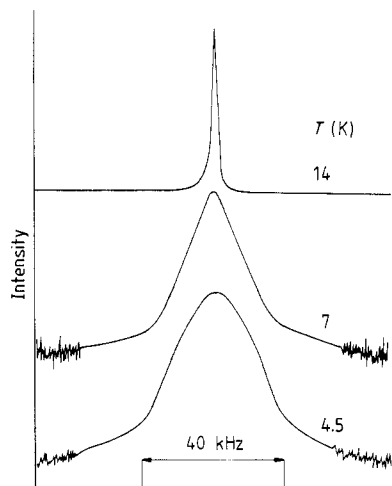
Since most attention was paid to the narrow line, such parameters as pulse repetition rate, spectral width, pulse width, etc were not optimum for the observation of the broad component. Nevertheless, figure 1 shows two spectra taken at 42 K and 4.3 K indicating remarkable changes in the narrow line (B) and essentially no change in the broad one. The temperature dependence of the linewidth of B and its shape at various temperatures are shown in figures 2 and 3, respectively. The B-curve broadens below about 10–11 K, and at  $T = 4.3$  K its shape exhibits a close similarity to the proton lineshape in solid hydrogen [7]. The second and fourth moments,  $m_2$  and  $m_4$ , were obtained from the data by fitting an analytic function

$$g(\nu) = \frac{1}{ab} \left( \frac{2}{\pi^3} \right)^{1/2} \int_{-b}^b \left[ 1 - \left( \frac{\alpha}{b} \right)^2 \right]^{1/2} \exp \left( \frac{-(\nu - \alpha)^2}{2a^2} \right) d\alpha \quad (1)$$

to the absorption spectra. This function was also used by Metzger and Gaines [8] in their lineshape analysis of solid hydrogen. The results  $m_2 = 75 \pm 5 \text{ kHz}^2$  and  $m_4 = (13.8 \pm 1.9) \times 10^4 \text{ kHz}^4$  were obtained. These are in good agreement with the data of Amstutz *et al* [9] which gave  $m_2 = 72.5 \text{ kHz}^2$  and  $m_4 = 12.5 \times 10^4 \text{ kHz}^4$  for solid HCP hydrogen at 4.0 K and 75% orthohydrogen concentration. As noted above, for  $T > 10$  K



**Figure 2.** Dependence of the linewidth of the narrow component (curve B in figure 1) on temperature. The linewidth is determined as full width at half maximum.



**Figure 3.** Examples of  $^1\text{H}$  NMR spectra at 14 K, 7 K and 4.5 K with the settings adjusted for observation of the narrow resonance line. The settings were: spectral width, 100 kHz; receiver bandwidth 2 MHz; repetition time 1 s; the number of transients was 360. The noise level is marked on both edges of the spectra. The small curvature of the base line seen on the  $T = 4.5$  K and  $T = 7$  K spectra is due to a weak background signal. It was subtracted before further reduction of the data, i.e. before determination of the moments and linewidths.

the B-linewidth is temperature dependent and can be associated with the proton self-diffusion processes characteristic of many metal-hydride systems as well as solid hydrogen. To analyse the data, we employ a formalism introduced by Hendrickson and Brey [10] which contains no model-dependent assumptions as to the physical origin of the motional-narrowing processes. An activation energy  $E_a$  of such a process can be obtained from the following relation:

$$\ln(1/\delta H - 1/\delta H_0) = -(E_a/kT) + \ln(1/B_0 - 1/\delta H_0) \quad (2)$$

where  $\delta H$  and  $\delta H_0$  are the measured and rigid-lattice linewidths and  $B_0$  is an assumed temperature-independent linewidth. In determining  $E_a$  from (2), the magnetic inhomogeneous broadening of order 0.5 kHz has been subtracted from the values of  $\delta H$  and  $\delta H_0$  and  $\delta H_0 = 24.5$  kHz was used. A least-squares fit of (2) to the data then yields  $E_a = 0.17$  kcal mol $^{-1}$  and  $B_0 = 0.08$  kHz. It is interesting to note that the activation energy determined in this way agrees well with the value estimated from a simple Waugh and Fedin [11] formula

$$E_a \approx 37 T_c \text{ cal mol}^{-1} \quad (3)$$

where  $T_c$  is the temperature of the onset of the line narrowing. Also, the application of the above relation to the solid hydrogen data, with  $T_c \approx 9$ – $10$  K [12], gives  $E_a$  close to 380 cal mol $^{-1}$  calculated from the temperature dependence of the spin-spin ( $T_2$ ) relaxation measurements [13]. The  $E_a$  value obtained here for the narrow resonance line is about half of that found for solid hydrogen [13], also by NMR techniques. This result may not be surprising in view of the different properties of surface hydrogen layer(s) compared with those of solid  $\text{H}_2$  alone. An activation energy equal to half that of solid  $\text{H}_2$  has been reported for a hydrogen monolayer adsorbed on carbon [14]. The smaller activation energy is probably a consequence of a coordination number lower than that in HCP solid hydrogen. In the monolayer each atom has fewer neighbours than in bulk  $\text{H}_2$  due to the transition from three- to two-dimensional character of the atomic array.

Barnes *et al* [4] estimated that the narrow component of the proton spectrum of  $\text{LaNi}_5\text{H}_x$  arises from less than full monolayer molecular hydrogen coverage. The rela-

tively intense signal is due to a large specific area of highly fractured particles of the hydride. It is likely that a similar situation pertains in our material. Then our observations are consistent with the assumption that the narrow resonance line originates from adsorbed hydrogen surface coverage.

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