Measurement of ^{1}H Knight Shift and Magnetic Susceptibility in Compressed Powder Samples of $TaH_{0.61}$

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Measurements of the Knight shift K_H and the magnetic susceptibility of $TaH_{0.61}$ on thin foils, prepared from $TaH_{0.61}$ powder at high pressure, are reported. It is shown that the method leads to useful results and is applicable to brittle materials for which compact samples are not available. Both, K_H and χ_v, are given for the hydrides TaH_x in the range $0 \leqq x \leqq 0.74$.

Introduction

A valuable experimental method in studying the band structure of metals and alloys is the measurement of the NMR shift of suitable nuclei with respect to a reference signal, the Knight shift (K), see e.g. [1]. Metal-hydrogen systems are an interesting group of metallic solids. The measurement of the proton Knight shift (K_H) in metals, however, is somewhat difficult because of its small magnitude, which is in the order of a few ppm.

Kazama and Fukai [2] were successful in studying K_H on thin metal foils MH_x by use of a continuous wave method (CW). Further improvement of the foil method was possible through application of pulsed NMR to systems MH_x [3, 4].

For many systems MH_x the difficulty of manufacturing thin foils arises because of the brittleness of the metal (alloy) of interest. Then the use of fine powder samples of MH_x is the only way for determining K_H. Within such samples large ^{1}H NMR line widths are observed, mainly due to the inhomogeneities of the magnetic induction at the sites of the nuclei considered. The origin of these inhomogeneities are the demagnetisation fields within the powder sample [5], created by the statistical distribution of the individual grains with respect to their shapes and orientations in reference to the applied induction $\boldsymbol{B}_0$. The contribution to the line width arising thereby is proportional to the volume susceptibility (χ_v) of the material MH_x studied, and proportional to B_0. It is found: $\Delta B_{\text{powder}} \approx 3\chi_v \cdot B_0$ [5, 6]. Another contribution to the line width of ^{1}H NMR in systems MH_x is the dipolar interaction between the nuclear spins in the material, particularly the proton-proton interaction.

In the system considered here, TaH_x, the ^{1}H NMR line width is narrowed considerably at temperatures above ~ 240 K, this effect being due to the high mobility of the hydrogen atoms (or protons) in the lattice (motional narrowing). Form the literature it is known that the line width $\Delta\nu$ of ^{1}H NMR in $TaH_{0.75}$, α-phase, is 3.5 kHz at a resonance frequency of 60 MHz [7]. This value of $\Delta\nu$ is many times larger than the ^{1}H Knight shift in this material as measured by the foil method [2, 4]. The shift of the ^{1}H NMR in MH_x is also influenced by the pretreatment of the material. Schreiber and Graham [8] have shown a way to separate the influence of the demagnetisation field from K_H by using cylindrical samples of powdered metal hydride. However, the foil method is superior to the Schreiber-Graham method not only due to the higher resolution (accuracy) but also due to the fact that both, K_H and χ_v are found simultaneously in one experiment.

In the following it is shown that with compressed powder samples reliable data for χ_v and K_H can be obtained. The material used is $TaH_{0.61}$.

Experimental

Ta-powder (99.9% purity) with a particle size $d_{\max} < 40$ µm was charged with hydrogen in a set up described earlier [9]. By use of a hydraulic press the hydrogenated powder was compressed to disks of 13 mm diameter. With a sample weight of ≈ 100 mg the thickness of the disk was about 50 µm. By X-ray

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powder diffraction it was found that no loss of hydrogen occurred during the compression. Rectangular samples, ≈ 3.8 mm wide, were cut from the disks.

The ^{1}H NMR was measured with a Varian spectrometer CFT 20 at a frequency $\nu_0 = 79.54$ MHz and at $T = 70$ °C. The Fourier transform technique was applied. The compressed powder samples (called "foils" in the following) were fixed with two glass plates and a teflon frame within an NMR tube of 4 mm diameter. D_2O was the lock substance used and the impurities, H_2O and DHO, were sufficient to provide an ^{1}H NMR reference signal. It is important to avoid gas bubbles between the glass plates and the foil, which lead to a structure in the NMR signal. χ_v and K_H were found from the $\sin^2\theta$ dependence of the ^{1}H NMR shift with respect to the reference signal. A more detailed description of the method is given in [2, 3]. At fixed θ the spectrum was accumulated 5000 times in all measurements reported here.

Results and Discussion

In Fig. 1 ^{1}H NMR spectra of powder samples $TaH_{0.61}$ are shown for various pressures applied during the manufacturing of the samples: $5.6 \leqq P/\text{kbar} \leqq 22.6$. The angle θ is 90°. It is seen that with increasing pressure the signal to noise ratio increases strongly and the line width $\Delta\nu$ decreases.

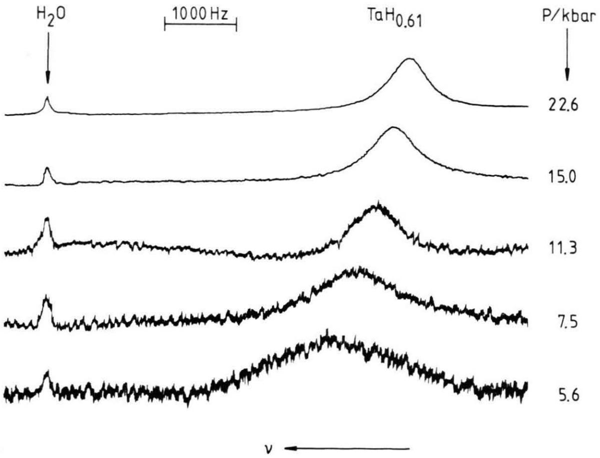

Fig. 1. ^{1}H NMR spectra of $TaH_{0.61}$, measured on thin foils prepared from powder at various pressures P. The angle θ between $\boldsymbol{B}_0$ and the surface of the foil is 90°. $T = 70$ °C; $\nu_0 = 79.54$ MHz; Number of sampling cycles: 5000.

The ^{1}H NMR shift S at constant induction B_0 is given by

$$S(\theta) = \left.\frac{\nu_{\text{foil}} - \nu_{H_2O}}{\nu_{H_2O}}\right|_{B_0=\text{const}}, \tag{1}$$

where ν_{foil} and ν_{H_2O} are the ^{1}H NMR frequencies of the TaH_x sample and the protons in the reference molecule H_2O, respectively. The angular dependence $S(\theta)$ is solely due to the demagnetisation field; one finds

$$S(\theta) = S(0) - 4\pi\left(1 - \frac{\pi}{8}\gamma + \frac{1}{8}\gamma^2\right) \cdot \sin^2\theta\,(\chi_{\text{v,foil}} - \chi_{\text{v},D_2O}) \,. \tag{2}$$

The demagnetisation field is determined by the difference in the volume susceptibilty χ_v of the foil, $\chi_{\text{v,foil}}$, and of the surrounding liquid D_2O, χ_{v,D_2O}. γ is the ratio of the thickness of the foil to its width.

The susceptibility of the foil increases with increasing density, that is with increasing pressure applied during the manfacturing. Thereby the ^{1}H NMR line position shifts to lower frequencies (at constant B_0) due to the proportionality between χ_v and the demagnetisation field (see (2)). In Figs. 2 and 3 ^{1}H NMR spectra of $TaH_{0.61}$ are given for various angles θ. One of the foils was made under a pressure of 7.5 kbar, the other one under $P = 22.6$ kbar.

With $\chi_{\text{v},D_2O} = -0.71 \cdot 10^{-6}$, $\chi_{\text{v,foil}}$ can be calculated from (2). For a quantitative evaluation of χ_v and K_H we introduce the ratio $f = \varrho_{\text{foil}}/\varrho_{\text{bulk}}$. The density of the foil (ϱ_{foil}) can be determined from the mass and the known geometry of the sample. To calculate f and the mass susceptibility χ_g the bulk density of TaH_x, ϱ_{bulk}, has to be known. Since no data are available on $\varrho(TaH_x)$ in the literature, the bulk density of $TaH_{0.61}$ was estimated in the following way: From the X-ray diffraction data a density ϱ_x of 15.3 g cm^{-3} was calculated. ϱ_x is mostly larger than the pycnometric density (here $\varrho_{\text{pyc}} = \varrho_{\text{bulk}}$), this effect being due to lattice defects. To correct for this difference of ϱ_{bulk} and ϱ_x, it was assumed that the effect of defects on ϱ in $TaH_{0.61}$ would be similar to TiH_2, for which an enhancement of ϱ_x of 5% is found in comparison to ϱ_{bulk}. Applying the appropriate correction one calculates $\varrho_{\text{bulk}}(TaH_{0.61}) = 14.6$ g cm^{-3}. The mass susceptibility χ_g is of course independent of the ratio f.

As mentioned above the Knight shift of the ^{1}H NMR in metals is small, and it naturally depends

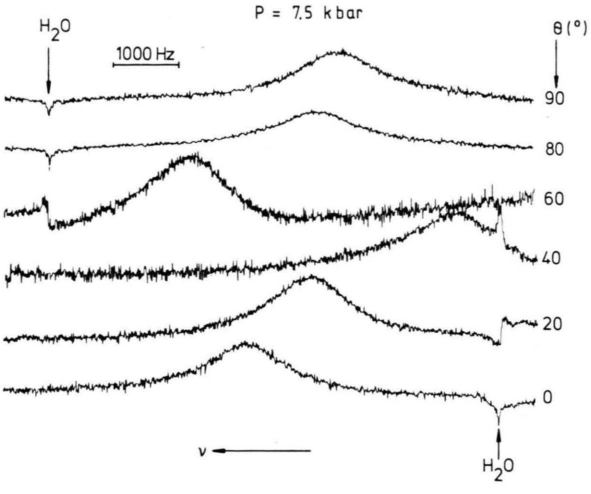

Fig. 2. ¹H NMR spectra of $TaH_{0.61}$, thin foil, for various angles θ ($P = 7.5$ kbar, $T = 70$ °C, $\nu_0 = 79.54$ MHz).

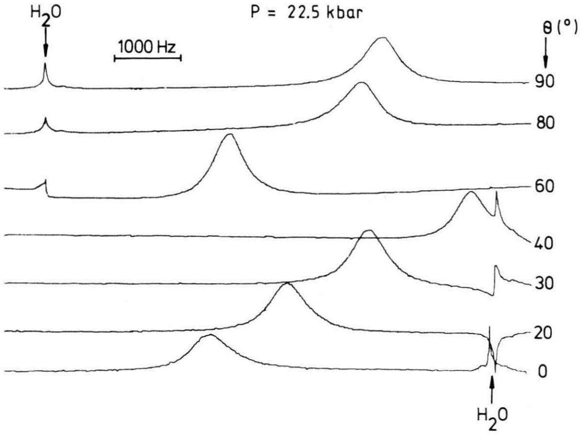

Fig. 3. ¹H NMR spectra of $TaH_{0.61}$, thin foil, for various angles θ ($P = 22.5$ kbar, $T = 70$ °C, $\nu_0 = 79.54$ MHz).

from the choice of the reference. It makes sense to refer to the bare proton as a reference point. Then

$$\frac{K_H}{\text{ppm}} = S(0) - \frac{4\pi}{3}(\chi_{v,\text{foil}} - \chi_{v,D_2O}) - 25.6. \quad (3)$$

The term $4\pi/3$ $(\chi_{v,\text{foil}} - \chi_{v,D_2O})$ takes the Lorentz field into account [10], and the shielding constant (shift) of the ¹H NMR of a proton in H_2O is 25.6 ppm with respect to the bare proton [11]. This means that the ¹H NMR frequency of the isolated proton is shifted 25.6 ppm with regard to the ¹H NMR signal of H_2O, this shift being to higher frequencies at constant B_0.

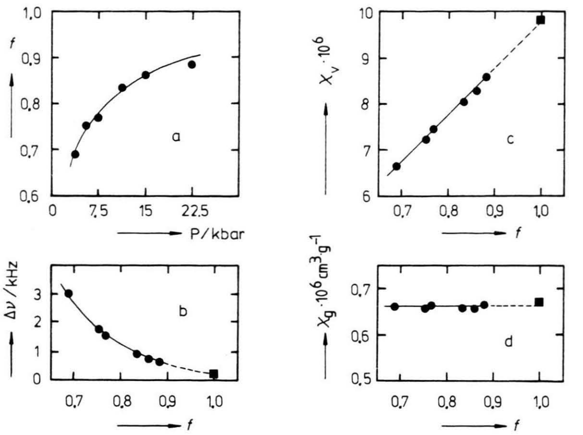

Fig. 4. a) Density factor $f = \varrho_{\text{foil}}/\varrho_{\text{bulk}}$ as a function of the pressure P applied during the production of the sample. b) Line width $\Delta\nu$ of the ¹H NMR signal as a function of f. c) Volume susceptibility χ_v of foils $TaH_{0.61}$ as a function of f. d) Mass susceptibility χ_g of $TaH_{0.61}$ as a function of f.

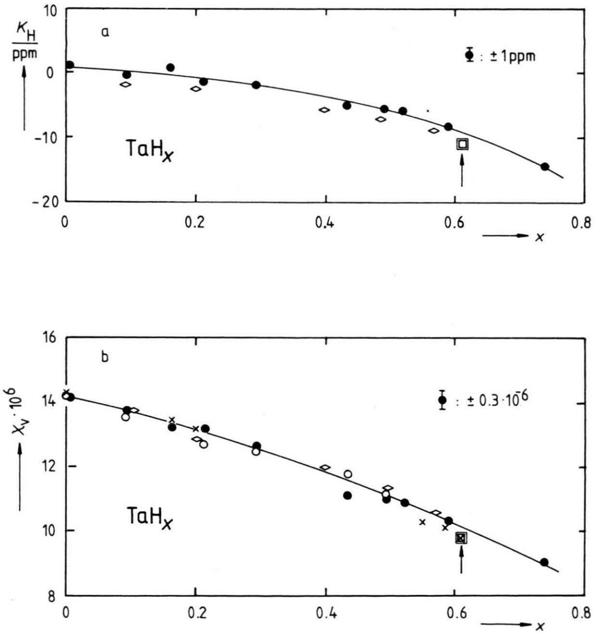

Fig. 5. a) ¹H NMR shift (Knight shift) K_H of TaH_x as a function of x. ●: this paper (pulse method), compact material; ◇: CW method [2]; ⊡: this paper, foil from compressed powder. b) χ_v of TaH_x as a function of x. ●: this paper (¹H NMR, pulse method, on compact foils), $T = 80$ °C; ◇: CW method [2]; ○: this paper, Faraday method at $T = 25$ °C; ×: Faraday method at $T = 25$ °C [12]; ⊡: this paper, from compressed powder, extrapolated to $f = 1$.

The density factor f increases with increasing preparation pressure P. $f = \varphi(P)$ is an individual constant of the material considered. In Fig. 4a $f = \varphi(P)$ is shown for $TaH_{0.61}$. As expected, with increasing f the line width decreases and thereby the signal to noise ratio (S/N) too, see Figure 4b. This is due to the decreasing spread of the demagnetisation field with increasing density of the foil, ϱ_{foil}. Foils prepared under a pressure of 22.6 kbar, however, show still a line width which is about four times larger than that of compact material. By extrapolation to $f = 1$ it is possible to determine $\chi_{v,compact}$ and $\Delta\nu_{compact}$. The extrapolated value is in good agreement with the data found for the compact material. This is shown in Fig. 5 where measurements of χ_V and K_H found with foils prepared by rolling Ta metal sheet and hydriding it thereafter are given together with data from the literature. For comparison the dependence of K_H on x for TaH_x is given too. For all measurements on foils of compressed powder, $K_H(TaH_{0.61})$ is found to be -11.4 ± 0.8 ppm, in good agreement with the data for compact material.

The volume susceptibility depends strongly on the density factor f (see Fig. 4c) whereas χ_g is independent of ϱ_{foil}, as expected. We find $\chi_g(TaH_{0.61}) = 0.66 \cdot 10^{-6}\,cm^3\,g^{-1}$.

Acknowledgement

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