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 $\chi_v$, are given for the hydrides TaH$_x$ in the range $0 \leq x \leq 0.74$.

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 $B_0$. The contribution to the line width arising thereby is proportional to the volume susceptibility ($\chi_v$) 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$_{0.61}$, 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 $\Delta V$ of $^1$H NMR in TaH$_{0.75}$ x-phase, is 3.5 kHz at a resonance frequency of 60 MHz [7]. This value of $\Delta V$ 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 $\chi_v$ are found simultaneously in one experiment.

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

Experimental

Ta-powder (99.9% purity) with a particle size $d_{\text{max}} < 40 \mu m$ 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 $\approx 100 \text{ mg}$ the thickness of the disk was about 50 $\mu m$. By X-ray

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powder diffraction it was found that no loss of hydrogen samples, \( \approx 3.8 \) mm wide, were cut from the disks.

The \(^1\text{H}\) NMR was measured with a Varian spectrometer CFT 20 at a frequency \( v_0 = 79.54 \) 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\(_2\)O was the lock substance used and the impurities, H\(_2\)O and DHO, were sufficient to provide an \(^1\text{H}\) 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. \( \chi_s \) and \( K_H \) were found from the \( \sin^2 \theta \) dependence of the \(^1\text{H}\) NMR shift with respect to the reference signal. A more detailed description of the method is given in [2, 3]. At fixed \( \theta \) the spectrum was accumulated 5000 times in all measurements reported here.

**Results and Discussion**

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

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

\[
S(\theta) = \frac{v_{\text{foil}} - v_{\text{H}_2\text{O}}}{v_{\text{H}_2\text{O}}}|_{B_0=\text{const}}
\]

where \( v_{\text{foil}} \) and \( v_{\text{H}_2\text{O}} \) are the \(^1\text{H}\) NMR frequencies of the TaH\(_x\) sample and the protons in the reference molecule H\(_2\)O respectively. The angular dependence \( S(\theta) \) is solely due to the demagnetisation field; one finds

\[
S(\theta) = S(0) - 4\pi \left( 1 - \frac{\pi}{8} + \frac{1}{8} \gamma^2 \right)
\]

The demagnetisation field is determined by the difference in the volume susceptibility \( \chi_v \) of the foil, \( \chi_{v,\text{foil}} \), and of the surrounding liquid D\(_2\)O, \( \chi_{v,\text{D}_2\text{O}} \); \( \gamma \) 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 manufacturing. Thereby the \(^1\text{H}\) NMR line position shifts to lower frequencies (at constant \( B_0 \)) due to the proportionality between \( \chi_v \) and the demagnetisation field (see (2)). In Figs. 2 and 3 \(^1\text{H}\) NMR spectra of TaH\(_{0.61}\) are given for various angles \( \theta \). One of the foils was made under a pressure of 7.5 kbar, the other one under \( P = 22.6 \) kbar.

With \( \chi_{v,\text{D}_2\text{O}} = -0.71 \cdot 10^{-6} \), \( \chi_{v,\text{foil}} \) can be calculated from (2). For a quantitative evaluation of \( \chi_v \) and \( K_H \) we introduce the ratio \( f = q_{\text{foil}}/q_{\text{bulk}} \). The density of the foil \( (q_{\text{foil}}) \) can be determined from the mass and the known geometry of the sample. To calculate \( f \) and the mass susceptibility \( \chi_g \) the bulk density of TaH\(_x\), \( q_{\text{bulk}} \), has to be known. Since no data are available on \( q \) (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 \( q_0 \) of 15.3 g cm\(^{-3}\) was calculated. \( q_0 \) is mostly larger than the pycnometric density (here \( q_{\text{pyc}} = q_{\text{bulk}} \)), this effect being due to lattice defects. To correct for this difference of \( q_{\text{bulk}} \) and \( q_0 \), it was assumed that the effect of defects on \( q \) in TaH\(_{0.61}\) would be similar to TiH\(_2\), for which an enhancement of \( q_0 \) of 5% is found in comparison to \( q_{\text{bulk}} \). Applying the appropriate correction one calculates \( q_{\text{bulk}} \) (TaH\(_{0.61}\)) = 14.6 g cm\(^{-3}\). The mass susceptibility \( \chi_g \) is of course independent of the ratio \( f \).

As mentioned above the Knight shift of the \(^1\text{H}\) NMR in metals is small, and it naturally depends
from the choice of the reference. It makes sense to refer to the bare proton as a reference point. Then
\[
\frac{K_H}{\text{ppm}} = S(0) - \frac{4\pi}{3} \left( \chi_v, \text{foil} - \chi_v, \text{D}_2O \right) - 25.6. \tag{3}
\]
The term \(4\pi/3 \left( \chi_v, \text{foil} - \chi_v, \text{D}_2O \right)\) takes the Lorentz field into account [10], and the shielding constant (shift) of the \(^1\text{H}\) NMR of a proton in \(\text{H}_2\text{O}\) is 25.6 ppm with respect to the bare proton [11]. This means that the \(^1\text{H}\) NMR frequency of the isolated proton is shifted 25.6 ppm with regard to the \(^1\text{H}\) NMR signal of \(\text{H}_2\text{O}\), this shift being to higher frequencies at constant \(B_0\).
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, $q_{\text{foil}}$. 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 $\chi_v,_{\text{compact}}$ and $\alpha_{\text{compact}}$. The extrapolated value is in good agreement with the data found for the compact material. This is shown in Fig. 5 where measurements of $\chi_v$ 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 $-11.4 \pm 0.8$ ppm, in good agreement with the data for compact material.

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

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