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Titanium Knight shift in $Ti_{1-x}V_x$ ($0 \leqslant x \leqslant 0.65$) dihydrides

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Abstract

The titanium Knight shifts have been measured in the cubic and tetragonal phases of TiH_2 in the 155–320 K temperature range. The anisotropy of the Knight shift tensor of ^{49}Ti resonance in the tetragonal phase was determined. The axial Knight shift K_{ax} which was equal to $+0.0087 \pm 0.0005\%$ at 155 K decreased to $+0.0050 \pm 0.0005\%$ at 250 K.

The titanium Knight shifts in nearly stoichiometric dihydrides of $Ti_{1-x}V_x$ ($0.04 \leqslant x \leqslant 0.65$) alloys were measured at room temperature. They have decreased from $K = 0.245 \pm 0.002\%$ for pure TiH_2 ($x = 0$) to $K = 0.11 \pm 0.01\%$ in $Ti_{0.35}V_{0.65}H_{\approx 2}$. These changes are discussed in terms of the changes in the magnetic susceptibilities in these materials.

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1. Introduction

Although the nuclear magnetic resonance (NMR) active isotopes of titanium have some features which are unfavourable for experiment (relatively large electric quadrupole moments and low abundances) their resonances have been recently observed in both the cubic and the tetragonal phases in TiH_2 [1, 2]. Those experiments were performed at 16.9 MHz (7.05 T).

In the cubic phase both ^{47}Ti and ^{49}Ti resonance lines are symmetric in shape but thermally induced tetragonality introduces a distortion of the line shape which tentatively was attributed to quadrupole interactions.

The present investigation of the titanium NMR has been carried out, firstly, to explain the line shape changes in TiH_2 more accurately and, secondly, to study the Knight shift of titanium resonance in substitutional titanium-based alloys, such as $Ti_{1-x}V_xH_{\approx 2}$, which we have investigated previously [3, 4] by means of ^1H and ^{51}V NMR.

2. Experimental details

We report here the $^{47,49}Ti$ resonances in TiH_2 using the same sample as in ref. 2 and $Ti_{1-x}V_xH_{\approx 2}$ ($x = 0.04$, 0.08, 0.12, 0.16, 0.35 and 0.65) using the same samples as those in refs. 3 and 4, where a detailed description of the sample preparation, X-ray analysis, magnetic susceptibility, ^1H and ^{51}V NMR measurement results are given. For TiH_2 the X-ray diffraction measurements were performed using a Siemens powder diffractometer. The diffraction patterns were used to obtain the structure and lattice parameters. The data were taken in the 30–330 K temperature range.

The titanium resonances were observed at nominal frequency of 16.9 MHz on a Bruker MSL 300S spectrometer equipped with a B-VT 1000E temperature controller. The spectra obtained for TiH_2 are Fourier transforms of typically 6500 signals of free induction decays (FIDs) after a single pulse (5.25 μs). The length of the pulse corresponds to a 90° pulse for the reference sample of $TiCl_4$. The temperature was varied from 155 to 320 K. The Knight shifts were measured relative to $TiCl_4$ in which the ^{49}Ti nucleus resonates at a frequency of 266.2 ppm higher than that of ^{47}Ti [5]. Then both signals are separated by 4.5 kHz in a resonance field of 7.05 T.

The resonance absorption spectra for $Ti_{1-x}V_xH_{\approx 2}$ hydrides were obtained at room temperature (cubic phase) from the Fourier transforms of the spin echo, using a different probe head from that for FID recording in TiH_2. The lengths of the first and second pulses were 6.25 μs and 12.5 μs respectively. Depending on the titanium concentration in the sample investigated, up to about 300 000 repetitive scans were required to achieve an adequate signal-to-noise ratio. Since resolution of the ^{47}Ti from ^{49}Ti signals was not possible, the shifts were measured as the difference between the maximum of the recorded spectrum and the midpoint between the ^{47}Ti and ^{49}Ti resonances in $TiCl_4$. This

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gives a trend of the titanium resonance shift as a function of vanadium concentration.

3. Results and discussion

3.1. Titanium dihydride

Figure 1 shows the spectra for TiH_2 recorded at different temperatures. Two well-resolved signals at 320 K (cubic phase) are separated by 4.5 kHz. Exactly the same frequency difference is observed between ^{49}Ti and ^{47}Ti resonance lines in the reference sample of $TiCl_4$. Moreover, both lines in TiH_2 are symmetric and the measured full width at half-maximum (FWHM) equal to 1.6 kHz compares favourably with $M_2^{1/2} = 1.25$ kHz, where M_2 is the calculated second-moment value of the dipolar Ti–H coupling. Thus the observed signals in TiH_2 are attributed to the ^{49}Ti (on the left) and ^{47}Ti resonances. A quadrupolar broadening, if present, is very small.

In the tetragonal phase, with decreasing temperature, the spectra reveal two features (Fig. 1, spectra b–d): (1) a progressive shift to highest frequencies; (b) a progressive distortion of the line shape.

Usually, in non-cubic materials, quadrupolar interactions and Knight shift anisotropy may occur together and these effects ought to be treated simultaneously in interpreting the observed spectra. This is particularly important in the case of powder specimens. In the present case, the characteristic line shape and lack of satellite lines strongly indicate the importance of Knight shift anisotropy effects. A similar situation has been recently observed by us in the tetragonal ZrH_2 [6], for which both static and magic angle spinning (MAS) ^{91}Zr NMR experiments clearly indicated that the Knight shift anisotropy determines the line shape and the quadrupolar interactions can be neglected. As in ZrH_2, the axial Knight shift K_{ax} in TiH_2 is positive. Its values, together with the tetragonality parameter a/c, are presented in Fig. 2. One can see that K_{ax} increases with the increase in the a/c ratio.

If we neglect spin–orbit coupling, there are two contributions to K_{ax}, associated with the tetragonal lattice of TiH_2. One of them is the orbital contribution K_{ax}^{VV} due to possible magnetic susceptibility anisotropy and second K_{ax}^{dip} arises because of the spin–dipolar interaction. In the first case, we have [8]

$$K_{ax}^{VV} = \tfrac{1}{3}(K_{\parallel}^{VV} - K_{\perp}^{VV}) = \tfrac{1}{3}(\mu_B N)^{-1} H_{VV}(\chi_{\parallel} - \chi_{\perp}) \tag{1}$$

where N is Avogadro's number, μ_B is the Bohr magneton, H_{VV} is the orbital hyperfine field, and $\chi_{\parallel}$ and $\chi_{\perp}$ are the parallel and perpendicular components respectively of the orbital magnetic susceptibility. In turn for K_{ax}^{dip}, an axial crystal symmetry case, one has [9]

$$K_{ax}^{dip} = 2\mu_B^2 N(E_F)\bar{q}S \tag{2}$$

where $N(E_F)$ is the total electron density of states at the Fermi energy for one spin direction, S is the Stoner factor and $\bar{q} = a_p\langle r^{-3}\rangle_{p,\, E=E_F} + a_d\langle r^{-3}\rangle_{d,\, E=E_F}$, where the coefficients a_p and a_d are functions of the partial electron densities of states of appropriate symmetry. K_{ax}^{VV} and K_{ax}^{dip} can be positive as well as negative in sign. One can see from the above that further discussion of the

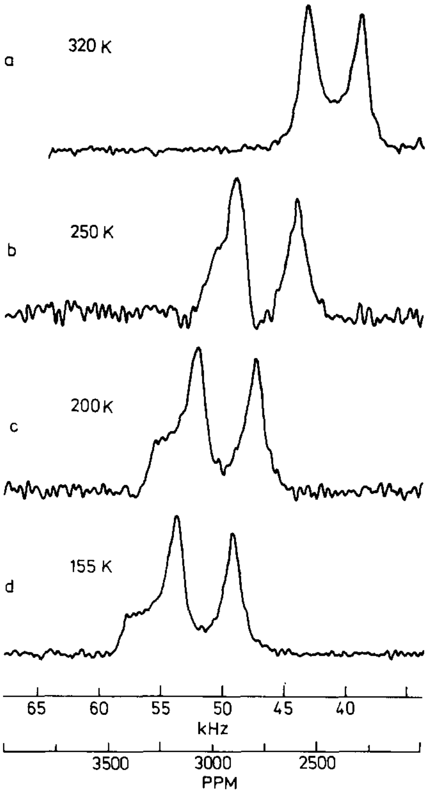

Fig. 1. Temperature evolution of absorption spectra of the ^{47}Ti and ^{49}Ti resonances in TiH_2.

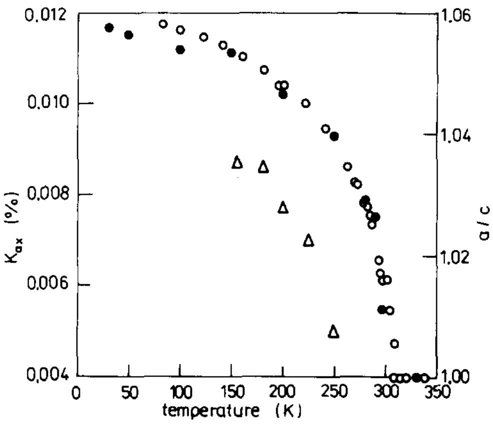

Fig. 2. Temperature dependencies of the axial Knight shift (Δ) and tetragonality parameter (●) in TiH_2. The a/c data for titanium dideuteride (○) are taken from ref. 7.

observed K_{ax} values requires knowledge of some details of electron band structure of the tetragonal TiH_2. This is not available at present and we have to postpone further analysis of K_{ax} until such information exists.

3.2. $Ti_{1-x}V_x$ alloy dihydrides

The $^{47,49}Ti$ NMR spectra are found to be very sensitive to vanadium concentration in $Ti_{1-x}V_x$ alloy hydrides. Even at a low vanadium content ($x=0.04$), both resonances of ^{47}Ti and ^{49}Ti are severely broadened (Fig. 3). However, their positions can still be distinguished. A further increase in vanadium causes overlapping of both signals to such an extent that they cannot be separated (Fig. 4). Although the hydrides still have cubic crystal symmetry, a random distribution of metal atoms reduces the point symmetry. This, in turn, leads to line broadening due to possible Knight shift anisotropy and quadrupolar interactions. In fact, in our spectra, besides the broadening of the central part of the resonance line, low intensity "bumps" are observed. The bumps may be expected because of the non-central ($-\frac{1}{2} \leftrightarrow \frac{1}{2}$) transitions of both isotopes. They merge together and superimpose themselves on the central line in such a way that the characteristic quadrupolar and anisotropy strength parameters cannot be extracted. The position of the maximum of resonance signal was taken as the reference point characterizing the Knight shift. The results of the Knight shift measurement in $Ti_{1-x}V_xH_{\approx 2}$ together with the bulk magnetic susceptibility data are listed in Table 1. The dependence of this shift K *vs.* bulk magnetic susceptibility χ with vanadium concentration x as the implicit parameter is shown in Fig. 5.

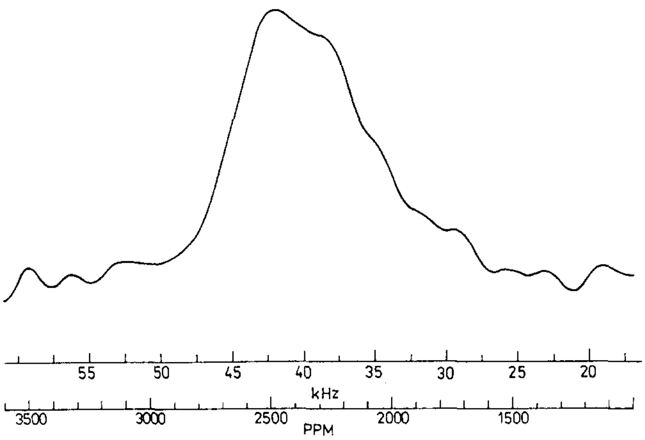

Fig. 3. The $^{47,49}Ti$ absorption spectrum in $Ti_{0.96}V_{0.04}H_{1.99}$ recorded at $T=294$ K using 111 112 scans.

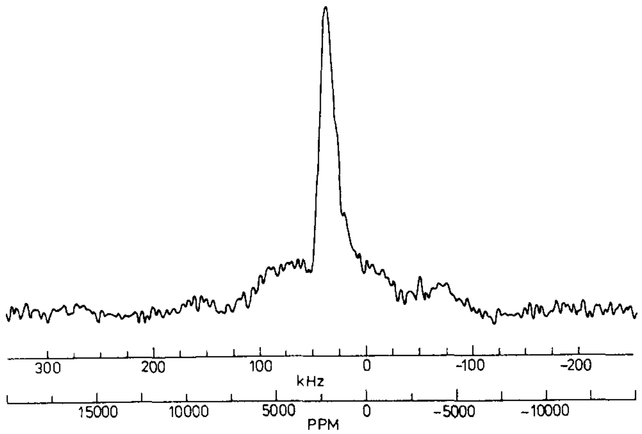

Fig. 4. The $^{47,49}Ti$ absorption spectrum in $Ti_{0.88}V_{0.12}H_{2.00}$ recorded at $T=294$ K with 174 000 scans. The strongly peaked central portion corresponds to the $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transitions of ^{47}Ti and ^{49}Ti. Zeros on both scales correspond to the position of ^{49}Ti resonance line in $TiCl_4$.

Most magnetic properties of transition metals can be understood on the basis of a two-band (s and d band) model. Within this model, the magnetic susceptibility may be written as

$$\chi=\chi_s+\chi_d+\chi_{VV}+\chi_{dia} \tag{3}$$

Here χ_s and χ_d represent the Pauli spin paramagnetic susceptibility of the s and d bands, respectively, χ_{dia} is the core diamagnetic and χ_{VV} is the orbital (Van-Vleck-type) paramagnetic susceptibility. Analogously, the Knight shift is given as the sum of various terms:

$$\begin{aligned} K &= K_s+K_d+K_{VV}+K_{dia} \\ &= (\mu_B N)^{-1}(\chi_s H_s+\chi_d H_{cp}+\chi_{VV} H_{VV})+K_{dia} \end{aligned} \tag{4}$$

where H_s, H_{cp} and H_{VV} are the s contact, d core polarization and d-orbital hyperfine fields respectively. This two-band model can also be applied to alloys and transition metal hydrides which are treated as interstitial alloys.

Thus the bulk susceptibility is given as the sum of the contributions of the components weighted by their respective concentrations. In our case of $Ti_{1-x}V_x$ dihydrides,

$$\chi=(1-x)\chi^{Ti}+x\chi^{V} \tag{5}$$

TABLE 1. Knight shift and magnetic susceptibility data obtained at 294 K for $Ti_{1-x}V_x$ dihydrides

x	K (%)	χ^b ($\times 10^{-6}$ emu mol^{-1})
0	$0.245^a \pm 0.002$	228
0.04	0.248 ± 0.005	224
0.08	0.235 ± 0.01	219
0.12	0.23 ± 0.01	224
0.16	0.23 ± 0.01	226
0.35	0.21 ± 0.01	212
0.65	0.11 ± 0.01	164

[a] Knight shift value for the cubic phase of TiH_2.

[b] Susceptibility value for TiH_2 ($x=0$) is taken from ref. 10, whereas the data for $Ti_{1-x}V_xH_{\approx 2}$ are taken from refs. 3 and 4.

TABLE 2. Summary of conduction electron contributions to the hyperfine fields, Knight shift and magnetic susceptibility for $Ti_{1-x}V_x$ dihydrides with $x=0.35$ and $x=0.65$, based on the procedure described in the text

x	χ_d ($\times 10^{-6}$ emu mol^{-1})	χ_{VV} ($\times 10^{-6}$ emu mol^{-1})	K_{cp} (%)	K_{VV} (%)	K_s[a] (%)	K_{dia}[a] (%)
0.35	97.5	118.0	−0.220	+0.378	+0.064	−0.010
0.65	87.3	80.2	−0.197	+0.257	+0.064	−0.010

$H_{cp}=-0.126\times10^6$ Oe and $H_{VV}=+0.179\times10^6$ Oe as used for TiH_2 [2].
[a]As used for TiH_2 [2].

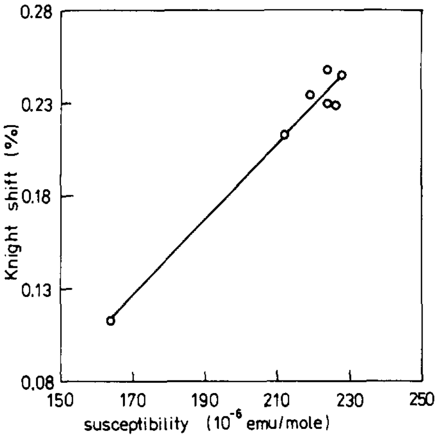

Fig. 5. The Knight shift K vs. bulk magnetic susceptibility χ in $Ti_{1-x}V_xH_{\approx 2}$ with the vanadium concentration x as the implicit parameter.

where χ^{Ti} and χ^{V} are expressed by eqn. (3).

In alloys, the main contributions, *i.e.* χ_d and χ_{VV} can be concentration dependent. In the vanadium-diluted alloys $Ti_{1-x}V_xH_{\approx 2}$ the ^{51}V NMR data analysis [4] indicated that the local vanadium susceptibility χ^V is larger than that of local titanium susceptibility if eqn. (5) is used. However, this excess decreases with increasing vanadium content and, for $x \geqslant 0.35$, one has $\chi \approx \chi^V \approx \chi^{Ti}$.

The hyperfine fields to a good approximation can be assumed to be concentration independent and their values can be taken to be the same as used by us previously in TiH_2 [2] NMR data analysis (Table 2).

A plot of K vs. χ (Fig. 5) shows a linear relation. The $\Delta K \Delta\chi$ experimental slope is positive and can be characterized by an effective hyperfine field H_{eff} equal to 0.114×10^6 Oe. This value can be related to appropriate changes in the χ components as a function of vanadium content x in the $Ti_{1-x}V_x$ alloys. In order to estimate them, we assume that the s contact and diamagnetic contributions to K and χ remain independent of x and defining

$$\Delta K = K(x=0) - K(x) \tag{6}$$

and

$$\Delta\chi = \chi(x=0) - \chi(x) = \Delta\chi_d^{Ti} + \Delta\chi_{VV}^{Ti} \tag{7}$$

one obtains:

$$\frac{\Delta K}{\Delta\chi} = (\mu_B N)^{-1} H_{eff}$$
$$= (\mu_B N)^{-1}\left((H_{cp} - H_{VV})\frac{\Delta\chi_d}{\Delta\chi} + H_{VV}\right) \tag{8}$$

Then, since $H_{eff} < H_{VV}$ (Table 2) and $H_{cp} - H_{VV} < 0$, it follows that $\Delta\chi_d/\Delta\chi \neq 0$. In other words, the observed decrease in K and χ with the increase in x should be attributed to a simultaneous reduction in both the d spin susceptibility χ_d^{Ti} and d orbital susceptibility χ_{VV}^{Ti}.

Using the magnetic susceptibility contributions in TiH_2 ($x=0$) evaluated earlier [2] and this procedure, we have partitioned measured values of K and χ into their contributions for $x=0.35$ and 0.65 (see Table 2). The results show that the changes in the magnetic susceptibility and the Knight shift are mainly due to the appropriate changes in d orbital contributions. Limited accuracy of the determination of the very small changes in K and χ values precludes similar analysis for the vanadium-diluted dihydrides.

References

1 S. D. Goren, C. Korn, H. Riesemeier, E. Rössler and K. Lüders, *Phys. Rev. B, 34* (1986) 6917.
2 B. Nowak, O. J. Żogał and K. Niedźwiedź, *J. Alloys Comp., 186* (1992) 53–64.
3 B. Nowak and M. Minier, *J. Less-Common Met., 101* (1984) 245.
4 B. Nowak, Y. Chabre and R. Andreani, *J. Less-Common Met., 130* (1987) 193.
5 N. Hao, B. G. Sayer, G. Dénès, D. G. Bickley, C. Detellier and M. J. McGlinchey, *J. Magn. Reson., 50* (1982) 50.
6 O. J. Żogał, B. Nowak and K. Niedźwiedź, *Solid State Commun., 82* (1992) 351.
7 H. L. Yakel, Jr., *Acta Crystallogr., 11* (1958) 46.
8 J. W. Ross, F. Y. Fradin, L. L. Isaacs and D. J. Lam, *Phys. Rev., 183* (1969) 645.
9 H. Ebert, J. Abart and J. Voitländer, *J. Phys. F, 16* (1986) 1287.
10 W. Trzebiatowski and B. Staliński, *Bull. Acad. Pol. Sci., 1* (1953) 131.