

## Nuclear magnetic resonance study of the electronic structure of $\text{TaV}_2\text{H}_x(\text{D}_x)$

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### Abstract

The magnetic susceptibilities,  $^1\text{H}$  and  $^{51}\text{V}$  Knight shifts and  $^{51}\text{V}$  spin–lattice relaxation rates in C15-type  $\text{TaV}_2\text{H}_x(\text{D}_x)$  ( $0 \leq x \leq 1.54$ ) have been studied as functions of temperature and hydrogen content. The density of d electron states at the Fermi level estimated from the experimental data is found to have a minimum near  $x=0.8$ . The effective hyperfine magnetic field at proton sites appears to be positive (*i.e.* parallel to the external field).

### 1. Introduction

Hydrogen-induced changes in the electronic spectra of intermetallic compounds have received much recent attention [1]. Studies of the electronic properties as functions of hydrogen content are often complicated by the precipitation of hydrogen-rich phases. However, for a number of the Laves phase compounds with hydrogen the homogeneous solid solution region is very broad, spanning the whole accessible range of hydrogen concentrations at room temperature (or slightly above it). Examples of such systems are C15-type  $\text{HfV}_2\text{H}_x(\text{D}_x)$  ( $x \leq 4$ ) and  $\text{ZrV}_2\text{H}_x(\text{D}_x)$  ( $x \leq 5$ ). Recent nuclear magnetic resonance (NMR) [2, 3] and heat capacity [4] studies have shown that for both these systems the H(D) concentration dependence of the density of electron states at the Fermi level,  $N(E_F)$ , exhibits a minimum near  $x=2$ . The aim of the present work is to investigate the behaviour of  $N(E_F)$  as a function of H(D) content in the C15-type compounds  $\text{TaV}_2\text{H}_x(\text{D}_x)$ .

$\text{TaV}_2$  is known to absorb considerable amounts of hydrogen, forming a continuous row of homogeneous solid solutions  $\text{TaV}_2\text{H}_x$  ( $x \leq 1.7$ ) [5]. For all  $x$  the C15 host metal structure is retained down to 80 K. However, the complete phase diagram of the  $\text{TaV}_2$ –H(D) system is still unknown and the possibility of some kind of hydrogen ordering at low temperatures is not excluded [6, 7]. Recently we have found [8, 9] an unusual localized motion of H(D) atoms in  $\text{TaV}_2\text{H}_x(\text{D}_x)$  which is not frozen on the NMR frequency scale even below 40 K.

Direct information on the variation in  $N(E_F)$  may be obtained from the analysis of magnetic susceptibility and NMR data [10]. Earlier measurements of the magnetic susceptibility  $\chi$  in C15-type  $\text{TaV}_2\text{H}_x$  ( $0 \leq x \leq 0.81$ ) [11] have

shown that in the studied range of  $x$  the value of  $\chi$  decreases with increasing hydrogen content. In the present work we report on studies of the  $^{51}\text{V}$  and  $^1\text{H}$  Knight shifts, the  $^{51}\text{V}$  spin–lattice relaxation rate and the magnetic susceptibility in  $\text{TaV}_2\text{H}_x(\text{D}_x)$  ( $0 \leq x \leq 1.54$ ).

## 2. Experimental details

The preparation and characterization of the  $\text{TaV}_2\text{H}_x(\text{D}_x)$  samples have been described elsewhere [8]. NMR measurements on powder samples were performed on a Bruker SXP pulse spectrometer at the frequencies 19.3 MHz ( $^{51}\text{V}$ ) and 90 MHz ( $^1\text{H}$ ). NMR spectra were recorded by integrating the echo signal and sweeping the magnetic field ( $^{51}\text{V}$ ) and by Fourier transforming the free-induction decay signal ( $^1\text{H}$ ). The  $^{51}\text{V}$  spin–lattice relaxation time  $T_1$  was determined from the recovery of the free-induction decay signal after the saturation pulse sequence. The magnetic susceptibility was measured by the Faraday method in a field of 5 kG.

## 3. Results

### 3.1. Magnetic susceptibility

In all the studied  $\text{TaV}_2\text{H}_x$  samples the magnetic susceptibility is found to increase by about 10% as the temperature decreases from 300 to 77 K. Similar temperature dependences of  $\chi$  have been observed earlier for  $\text{TaV}_2\text{H}_x$  with  $x=0$  [12] and with  $0 \leq x \leq 0.81$  [11]. In Fig. 1 we show the magnetic susceptibility at room temperature as a function of hydrogen content. It can be seen that the concentration dependence of  $\chi$  exhibits a minimum near  $x \approx 0.8$ . Our results are in reasonable agreement with those of Lynch *et al.* [11] for  $x \leq 0.81$ .

The non-monotonic  $x$  dependence of  $\chi$  is also manifested in the behaviour of the  $^1\text{H}$  NMR linewidth  $\Delta\nu$ . At room temperature the dipole–dipole interactions of  $^1\text{H}$  spins are averaged out due to the fast hydrogen diffusion [8] and  $\Delta\nu$  is determined by the distribution of demagnetization fields over the sample volume. Hence for identical shapes of the samples the linewidth should be proportional to the magnetic susceptibility. The concentration dependence of  $\Delta\nu$  at room temperature is found to have a minimum near  $x \approx 0.8$  (Fig. 2).

### 3.2. $^{51}\text{V}$ Knight shift and spin–lattice relaxation rate

For all the studied samples the observed  $^{51}\text{V}$  NMR spectra at  $T=300$  K are the typical powder patterns of a nuclear spin  $I = \frac{7}{2}$  with axially symmetric electric quadrupole interaction. Although the  $\text{TaV}_2\text{H}_x(\text{D}_x)$  compounds are non-stoichiometric with respect to H(D) content, the quadrupole satellites in the room temperature  $^{51}\text{V}$  NMR spectra are well resolved owing to the fast hydrogen diffusion [13]. The central lines in the spectra show no signs

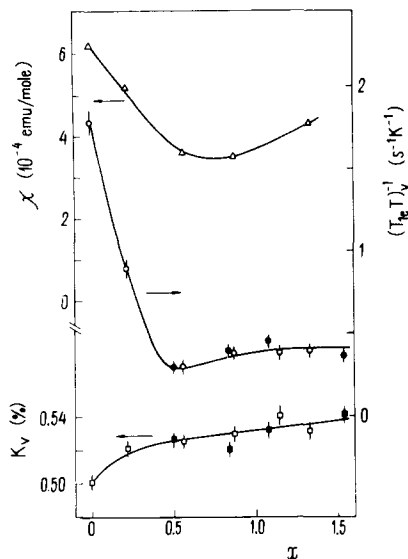


Fig. 1. Magnetic susceptibility ( $\Delta$ ), electronic contribution to  $^{51}\text{V}$  spin-lattice relaxation rate ( $\circ$ ,  $\bullet$ ) and  $^{51}\text{V}$  Knight shift ( $\square$ ,  $\blacksquare$ ) in  $\text{TaV}_2\text{H}_x(\text{D}_x)$  as functions of H(D) content. The open symbols correspond to hydrides and the filled ones to deuterides. The full lines are guides to the eye.

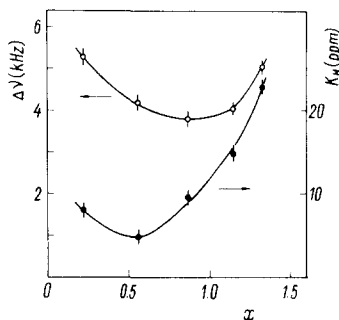


Fig. 2. Proton NMR linewidth ( $\circ$ ) and proton Knight shift ( $\bullet$ ) in  $\text{TaV}_2\text{H}_x$  as functions of hydrogen content. The full lines are guides to the eye.

of splitting. The  $^{51}\text{V}$  Knight shift values  $K_V$  have been determined from the positions of the central line maxima with respect to the  $^{51}\text{V}$  resonance line in an aqueous solution of  $\text{LiVO}_3$ . The measured  $^{51}\text{V}$  Knight shift at room temperature as a function of H(D) content is shown in Fig. 1. Note that the  $x$  dependence of  $K_V$  in  $\text{TaV}_2\text{H}_x(\text{D}_x)$  resembles the corresponding dependence in  $\text{HfV}_2\text{H}_x(\text{D}_x)$  [2, 3], although the  $K_V$  variation in the latter system is stronger. For all the studied samples the measured  $K_V$  values are temperature independent within our experimental accuracy.

For the  $\text{TaV}_2\text{H}_x(\text{D}_x)$  compounds with  $x > 0$  the observed  $^{51}\text{V}$  spin-lattice relaxation can be fitted by an exponential function. For the hydrogen-free  $\text{TaV}_2$  we have found deviations from the single-exponential recovery. This may be related to the fact that  $\text{TaV}_2$  has the highest  $^{51}\text{V}$  quadrupole interaction parameter within the  $\text{TaV}_2\text{H}_x(\text{D}_x)$  series [13] and therefore it is more difficult to achieve complete saturation of all the nuclear transitions in  $\text{TaV}_2$ . In order to estimate the values of  $T_1$  for  $\text{TaV}_2$ , we have used the longest component of the observed relaxation curve.

The measured relaxation rate  $T_1^{-1}$  in metal-hydrogen systems usually results from the sum of contributions due to conduction electrons ( $T_{1e}^{-1}$ ) and the effects of H(D) motion on magnetic dipole ( $T_{1d}^{-1}$ ) and electric quadrupole ( $T_{1Q}^{-1}$ ) interactions:

$$T_1^{-1} = T_{1e}^{-1} + T_{1d}^{-1} + T_{1Q}^{-1} \quad (1)$$

As discussed in our previous papers [8, 9], the motional contributions to the relaxation rate in  $\text{TaV}_2\text{H}_x(\text{D}_x)$  show the double-peak temperature dependence originating from the effects of the localized motion and the long-range diffusion of H(D) atoms. The conduction electron contribution can be directly obtained from the experimental  $T_1^{-1}(T)$  data in the regions where the motional contributions are negligible, *e.g.* at very low temperatures and/or between the two peaks. In all the studied compounds with  $x > 0$   $T_{1e}^{-1}$  is found to be proportional to temperature as in ordinary metals. The resulting values of  $(T_{1e}T)_V^{-1}$  for different samples are presented in Fig. 1. For  $\text{TaV}_2$  the only important contribution to the relaxation rate is  $T_{1e}^{-1}$ ; however, the value of  $(T_{1e}T)_V^{-1}$  shows a weak temperature dependence. Included in Fig. 1 is the low temperature ( $T = 11$  K) value of  $(T_{1e}T)_V^{-1}$  for  $\text{TaV}_2$ . As can be seen from Fig. 1, we have not observed any effects of hydrogen isotope substitution on  $K_V$  and  $(T_{1e}T)_V^{-1}$  within our experimental accuracy.

### 3.3. Proton Knight shift

The values of the proton Knight shift have been determined from  $^1\text{H}$  NMR spectra at room temperature,  $\text{H}_2\text{O}$  serving as the reference substance. We have corrected the data for demagnetization effects in powder samples. The additional shift  $\delta H/H$  resulting from demagnetizing fields can be estimated using the expressions derived in ref. 14 and the experimental  $\chi$  data. The corrected values of the shift  $K_H$  (with respect to bare protons) for different samples are presented in Fig. 2. It should be noted that the corrections are considerably lower than the range of  $K_H(x)$  variations. In contrast to the proton Knight shift data for  $\text{HfV}_2\text{H}_x$  and  $\text{ZrV}_2\text{H}_x$  [2, 3], the  $K_H$  values for  $\text{TaV}_2\text{H}_x$  are positive.

As discussed in ref. 9, the electronic contribution to the proton relaxation rate could not be reliably determined from the experimental data because of the large motional contributions to the proton  $T_1^{-1}$  down to very low temperatures.

## 4. Discussion

The magnetic susceptibility of a transition metal compound usually consists of three main contributions:

$$\chi = \chi_s + \chi_{\text{orb}} + \chi_d \quad (2)$$

where  $\chi_s$  and  $\chi_d$  are the spin susceptibilities of s and d electrons respectively and  $\chi_{\text{orb}}$  is the orbital susceptibility of d electrons. The spin contributions are directly related to the corresponding densities of electron states at the Fermi level,  $N_s(E_F)$  and  $N_d(E_F)$ ; for instance,

$$\chi_d = 2\mu_B^2 N_A \frac{N_d(E_F)}{1 - JN_d(E_F)} \quad (3)$$

where  $\mu_B$  is the Bohr magneton,  $N_A$  is the Avogadro number and  $J$  is the electron-electron interaction parameter. The value of  $N_d(E_F)$  is usually much

higher than  $N_s(E_F)$ , *i.e.*  $\chi_d \gg \chi_s$ . Thus, in order to estimate the density of electron states at the Fermi level, it is necessary to separate the contributions  $\chi_{orb}$  and  $\chi_d$ . In favourable cases this can be done using the experimental data on the Knight shift and nuclear spin–lattice relaxation rate [10, 15]. For metal nuclei both  $K$  and  $(T_{1e}T)^{-1}$  are determined by sums of the same contributions as  $\chi$  and in the tight-binding approximation may be written as [16]

$$K = K_s + K_{orb} + K_d = \frac{1}{\mu_B N_A} (H_s \chi_s + H_{orb} \chi_{orb} + H_d \chi_d) \quad (4)$$

$$(T_{1e}T)^{-1} = (T_{1e}T)_s^{-1} + (T_{1e}T)_{orb}^{-1} + (T_{1e}T)_d^{-1} \\ = 2h\gamma^2 k_B [H_s^2 N_s^2(E_F) + (pH_{orb}^2 + qH_d^2) N_d^2(E_F)] \quad (5)$$

where  $H_s$ ,  $H_{orb}$  and  $H_d$  are the appropriate hyperfine fields at nuclear sites and  $\gamma$  is the nuclear gyromagnetic ratio. The dimensionless factors  $p$  and  $q$  (not exceeding unity) are determined by admixture coefficients of different  $d$  orbital states at the Fermi level [16].

We now estimate the parameters entering eqns. (2)–(5). For a small  $s$  contribution to  $\chi$  we use the value  $\chi_s = 0.2 \times 10^{-4}$  e.m.u. mole<sup>-1</sup> [17] corresponding to the free-electron model. Using the atomic value of the contact hyperfine field in vanadium,  $H_s = 1.6 \times 10^6$  Oe (per electron) [18], we obtain  $K_s = 0.1\%$ . Since both  $\chi$  and  $K_V$  in  $TaV_2H_x(D_x)$  are found to be nearly temperature independent, the core polarization hyperfine field  $H_d$  cannot be determined directly from the standard  $K$ - $\chi$  diagram. Therefore we make use of the value  $H_d = -1.2 \times 10^5$  Oe derived for vanadium in the related compound  $HfV_2$  [17]. We also adopt the atomic value of the orbital hyperfine field in vanadium,  $H_{orb} = 2.5 \times 10^5$  Oe [18], as an estimate of  $H_{orb}$  in our system. Assuming that the hyperfine fields at vanadium sites remain unchanged in the studied range of  $x$ , we can determine  $\chi_{orb}$ ,  $\chi_d$ ,  $K_{orb}$  and  $K_d$  from eqns. (2) and (4). The results for a number of compositions are presented in Table 1. It can be seen that the value of  $\chi_d$  shows a minimum as a function of  $x$ . The dominant contribution to the <sup>51</sup>V Knight shift is

TABLE 1

Observed values of magnetic susceptibility and <sup>51</sup>V Knight shift at room temperature and estimated orbital and d spin contributions to these values

Sample	$\chi^{obs}$ ( $10^{-4}$ e.m.u. mol <sup>-1</sup> )	$\chi_{orb}$	$\chi_d$	$K_V^{obs}$ (%)	$K_{orb}$	$K_d$
TaV <sub>2</sub>	6.20 ± 0.02	3.33	2.67	0.501 ± 0.005	0.497	-0.096
TaV <sub>2</sub> H <sub>0.22</sub>	5.20 ± 0.01	3.24	1.76	0.522 ± 0.005	0.486	-0.064
TaV <sub>2</sub> H <sub>0.56</sub>	3.62 ± 0.01	2.96	0.46	0.525 ± 0.005	0.442	-0.017
TaV <sub>2</sub> H <sub>0.87</sub>	3.52 ± 0.01	2.95	0.37	0.529 ± 0.005	0.442	-0.013
TaV <sub>2</sub> H <sub>1.33</sub>	4.32 ± 0.02	3.12	1.00	0.531 ± 0.006	0.467	-0.036

found to be the orbital one. This may account for the absence of an extremum in the concentration dependence of the measured Knight shift.

In order to obtain the bare density of d electron states at the Fermi level,  $N_d(E_F)$ , from eqn. (3), we have to estimate the electron–electron interaction parameter  $J$ . As for the  $\text{HfV}_2\text{H}_x(\text{D}_x)$  and  $\text{ZrV}_2\text{H}_x(\text{D}_x)$  systems [2], we adopt the value  $J=0.2$  eV, which is close to the one derived from the analysis of experimental data for  $\text{V}_3\text{Si}$  [19]. The resulting  $x$  dependence of  $N_d(E_F)$  (in units of states per electronvolt, metal atom and one spin direction) is shown in Fig. 3. In order to verify that the derived  $N_d(E_F)$  values are consistent with the other experimental results, we also employ the  $^{51}\text{V}$  relaxation rate data. Using the above-specified values of  $\chi_s$  and  $H_s$ , we obtain  $(T_{1e}T)^{-1} \approx 0.2 \text{ s}^{-1} \text{ K}^{-1}$ . If we replace the factors  $p$  and  $q$  by their maximum values (equal to unity), we can determine from eqn. (5) the lower boundary of the density of d electron states at the Fermi level,  $[N_d(E_F)]_{\min}$ . The resulting values of  $[N_d(E_F)]_{\min}$  appear to be 1.2–1.8 times lower than the corresponding values of  $N_d(E_F)$  derived from  $\chi_d$ . This is a reasonable result, since the typical values of  $p$  and  $q$  in transition metals are in the range 0.3–0.7 [16].

Band structure calculations are presently available only for the hydrogen-free compound  $\text{TaV}_2$ ; the resulting theoretical  $N(E_F)$  value is 0.43 states per electronvolt atom spin [20]. This is about two times lower than the  $N_d(E_F)$  value derived from our experiments. On the other hand, from the heat capacity data for  $\text{TaV}_2$  [12] and the electron–phonon coupling parameter  $\lambda=0.69$  [20], as estimated from the McMillan equation, one can obtain  $N(E_F)=1.22$  states per electronvolt atom spin, in reasonable agreement with our  $N_d(E_F)$  value. Similar problems are found to be typical for vanadium-based A15 and C15 compounds [20]: although the  $N(E_F)$  values derived from different experiments agree with each other, they are considerably higher than those obtained from band structure calculations. The discrepancies may arise from inadequate description of the electron correlations in these compounds.

Although the detailed theory of hyperfine interactions of hydrogen dissolved in a metal is lacking, the experimental data on proton Knight shifts in transition metal hydrides [21–24] unambiguously show that  $K_H$  is determined mainly by the density of d electron states at the Fermi level. Sorting out the  $N_d(E_F)$ -dependent term, we may write  $K_H$  in a form analogous to eqn. (4):

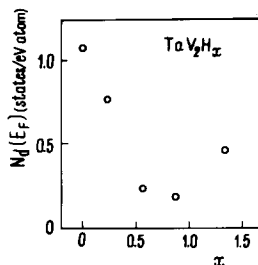


Fig. 3. Density of d electron states at the Fermi level as a function of hydrogen content.

$$K_H = K_0 + \frac{1}{\mu_B N_A} \tilde{H}_d \chi_d \quad (6)$$

where  $\tilde{H}_d$  is the effective hyperfine field at a proton site due to d electrons.

Comparison of the concentration dependences of  $\chi_d$  and  $K_H$  shows that  $\tilde{H}_d$  is expected to be positive, in contrast to the cases of  $\text{HfV}_2\text{H}_x$  and  $\text{ZrV}_2\text{H}_x$  where the values of  $\tilde{H}_d$  are found to be negative [2]. This indicates that the spin (and probably charge) distribution near protons in  $\text{TaV}_2\text{H}_x$  differs significantly from those in  $\text{HfV}_2\text{H}_x$  and  $\text{ZrV}_2\text{H}_x$ . It is interesting to note that for hydrogen in random b.c.c. Ta–V alloys the value of  $\tilde{H}_d$  appears to be negative [25]. Among the studied solid solutions of hydrogen in IVb and Vb metals and their b.c.c. alloys [25], positive  $\tilde{H}_d$  is found only for  $\text{TaH}_x$ ,  $\text{NbH}_x$  and  $\text{Nb}_{0.5}\text{Ta}_{0.5}\text{H}_x$ . It should be kept in mind, however, that the numerical values of  $\tilde{H}_d$  can hardly be obtained from the concentration dependences of  $\chi$  and  $K_H$ , since in metal–hydrogen systems both  $K_0$  and  $\tilde{H}_d$  may change with hydrogen content. More reliable estimates of  $\tilde{H}_d$  can be obtained for the systems where  $\chi$  and  $K_H$  show pronounced temperature dependences [23, 24].

## 5. Conclusions

The density of d electron states at the Fermi level estimated from the magnetic susceptibility and  $^{51}\text{V}$  Knight shift data for C15-type  $\text{TaV}_2\text{H}_x(\text{D}_x)$  shows a minimum near  $x \approx 0.8$ . This conclusion is also consistent with the  $^{51}\text{V}$  relaxation rate and proton Knight shift data. Similar  $x$  dependences of  $N_d(E_F)$  have been observed for the related C15-type compounds  $\text{HfV}_2\text{H}_x(\text{D}_x)$  and  $\text{ZrV}_2\text{H}_x(\text{D}_x)$  [2, 3]. However, in contrast to  $\text{HfV}_2\text{H}_x$  and  $\text{ZrV}_2\text{H}_x$ , the effective hyperfine magnetic field at proton sites in  $\text{TaV}_2\text{H}_x$  appears to be positive.

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