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LETTER TO THE EDITOR

NMR evidence for low-frequency local motion of H (D) atoms in TaV₂ at low temperatures

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Abstract. Measurements of the temperature dependence of the ¹H, ²D and ⁵¹V spin–lattice relaxation rates T_1^{-1} in TaV₂H_x (D_x) show a second low-temperature T_1^{-1} maximum in addition to the usual maximum associated with H(D) diffusion. This feature can be attributed to low-frequency local motion of H (D) atoms. Strong effects of hydrogen isotope substitution are observed at low temperatures.

Measurements of the nuclear spin–lattice relaxation time T_1 are widely used to study the motion of hydrogen atoms in metal–hydrogen systems (Seymour 1982). For thermally activated diffusive motion the $T_1^{-1}(T)$ maximum is usually observed when $\omega\tau_d \approx 1$, where $\omega/2\pi$ is the nuclear magnetic resonance (NMR) frequency, and τ_d is the mean dwell time of an H atom in an interstitial site. In the present Letter we report on the observation of an additional low-temperature T_1^{-1} maximum in the TaV₂–H (D) system. This feature is manifested in the temperature dependences of ¹H, ²D and ⁵¹V relaxation rates, and shows strong isotope effects. The additional T_1^{-1} maximum can be attributed to low-frequency local motion of H (D) atoms.

The C15-type intermetallic compound TaV₂ was prepared by arc melting the appropriate amounts of high-purity metals in an argon atmosphere with subsequent annealing in vacuum at 950 °C for 100 h. The samples were charged with H₂ (D₂) gas at a pressure of about 1 bar using a Sieverts-type vacuum system, and the H (D) content was determined from the hydrogen pressure change in the calibrated volume of the system. Measurements were made on the powdered samples of TaV₂H_x ($x = 0.56, 0.70, 0.87, 1.15$ and 1.33) and TaV₂D_x ($x = 0.50, 0.84, 1.08$ and 1.54). X-ray diffraction studies have shown that all the samples are single-phase solid solutions with the cubic C15-type host-metal structure. Our room-temperature structural data are consistent with those of Lynch (1981) and Somenkov and Irodova (1984a, b). The single-phase state with the C15 host structure is retained down to 80 K. According to the neutron diffraction data (Somenkov and Irodova 1984a, b) hydrogen atoms in TaV₂ occupy only tetrahedral interstitial sites of the g type, formed by 2V and 2Ta atoms.

NMR measurements were performed on a Bruker SXP pulse spectrometer at $\omega/2\pi = 13.8$ MHz (²D), 19.3 MHz (⁵¹V), 31, 64 and 90 MHz (¹H). Spin–lattice relaxation times were determined from the recovery of free-induction decay after the saturation pulse sequence (⁵¹V) or after the single RF pulse (¹H and ²D). In all cases the relaxation was single-exponential.

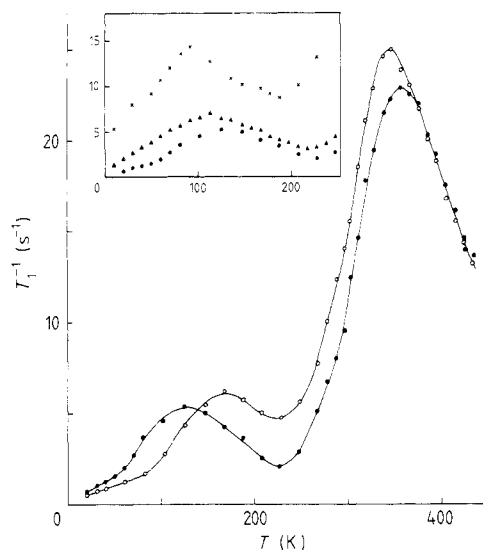


Figure 1. The temperature dependence of the ^1H spin-lattice relaxation rate in $\text{TaV}_2\text{H}_{0.87}$ (●) and $\text{TaV}_2\text{H}_{1.15}$ (○) measured at 90 MHz. Full curves are guides to the eye. Inset: the low-temperature part of the temperature dependence of $(T_1^{-1})_{\text{H}}$ in $\text{TaV}_2\text{H}_{0.87}$ at the frequencies 31 (×), 64 (▲) and 90 MHz (●).

The measured temperature dependences of ^1H spin-lattice relaxation rates in $\text{TaV}_2\text{H}_{0.87}$ and $\text{TaV}_2\text{H}_{1.15}$ at $\omega/2\pi = 90$ MHz are shown in figure 1. The similar double-peak $T_1^{-1}(T)$ dependences are observed for all the TaV_2H_x samples studied. As the hydrogen concentration increases the position of the high-temperature $(T_1^{-1})_{\text{H}}$ maximum shifts to lower T , and that of the low-temperature one shifts to higher T . The behaviour of ^1H NMR linewidths indicates that the high-temperature $(T_1^{-1})_{\text{H}}$ maximum is due to the diffusive motion of H atoms. Above 230 K the nuclear dipole-dipole interaction is dynamically averaged to zero, and ^1H NMR linewidths are determined only by distributions of demagnetising fields over sample volume.

The low-temperature $(T_1^{-1})_{\text{H}}$ maximum is also related to some kind of motion with the characteristic frequency $1/\tau_L \approx \omega$. This is supported by the behaviour of $(T_1^{-1})_{\text{H}}$ at different frequencies (see the inset of figure 1), typical for motionally induced relaxation. However, this motion cannot be identified as the long-range diffusion since the low- T maximum relaxation rate $(T_1^{-1})_{\text{H}}^{\text{L}T^{\text{max}}}$ indicates that only a part of the rigid-lattice dipole-dipole interaction is modulated by the motion. Thus, it may be concluded that some kind of low-frequency local motion of H atoms is present in TaV_2H_x at low temperatures.

This conclusion is consistent with the results of ^{51}V spin-lattice relaxation measurements shown in figures 2 and 3. As in the other vanadium-based Laves-phase hydrides (Belyaev *et al* 1983, 1984, Skripov *et al* 1987) the mechanism responsible for the observed high values of ^{51}V relaxation rates in TaV_2H_x (D_x) is the electric quadrupole interaction modulated by H (D) motion. As can be seen from figures 2 and 3, the Korringa contribution to $(T_1^{-1})_{\text{V}}$ proportional to T may be important only below 50 K and near 200 K. The double-peak temperature dependence of $(T_1^{-1})_{\text{V}}$ is observed for all the TaV_2H_x (D_x) samples studied. The positions of the $(T_1^{-1})_{\text{V}}$ maxima are consistent with the corresponding $(T_1^{-1})_{\text{H}}$ data. Therefore, the high- T $(T_1^{-1})_{\text{V}}$ maximum can be attributed to long-range H (D) diffusion, and the low- T one can be ascribed to the local motion of H (D) atoms. It has been noted by Belyaev *et al* (1984) that relaxation rate measurements on host-metal nuclei may serve as the basis of an efficient technique for studying isotope effects in hydrogen motion. Since the quadrupole interaction is

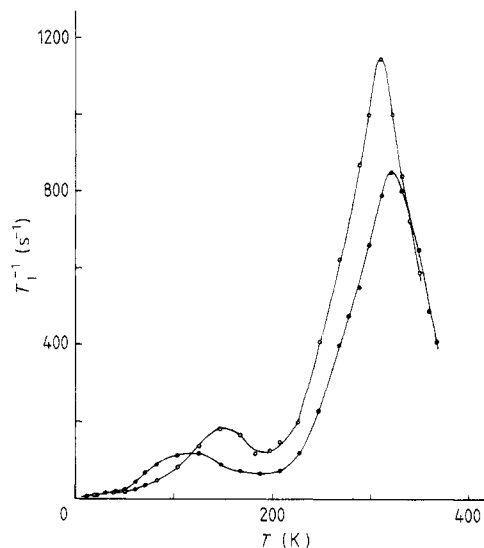


Figure 2. The temperature dependence of the ^{51}V spin-lattice relaxation rate in $\text{TaV}_2\text{H}_{0.87}$ (●) and $\text{TaV}_2\text{H}_{1.33}$ (○) measured at 19.3 MHz. Full curves are guides to the eye.

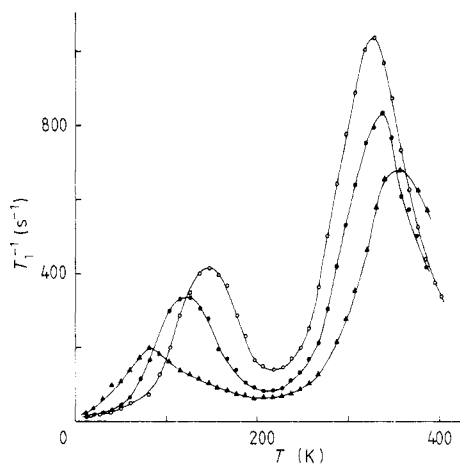


Figure 3. The temperature dependence of the ^{51}V spin-lattice relaxation rate in $\text{TaV}_2\text{D}_{0.50}$ (▲), $\text{TaV}_2\text{D}_{0.84}$ (●) and $\text{TaV}_2\text{D}_{1.08}$ (○) measured at 19.3 MHz. Full curves are guides to the eye.

determined by electronic and ionic charge distributions, H and D atoms are expected to give the same contributions to $(T_1^{-1})_V$ if their motional parameters are the same. The observed small relative shifts of the positions of high- T $(T_1^{-1})_V$ maxima for the hydrides and the deuterides with similar values of x indicate that the diffusion parameters of H and D atoms do not differ much near 300 K.

The most remarkable feature of the ^{51}V relaxation data is the strong effect of hydrogen isotope substitution on the measured $(T_1^{-1})_V$ in the low-temperature region. The high- T maximum relaxation rates $(T_1^{-1})_V^{\text{HTmax}}$ for the hydrides and the deuterides with similar values of x are nearly the same, as expected. However, the low- T maximum relaxation rates $(T_1^{-1})_V^{\text{LTmax}}$ for the deuterides are almost three times higher than the corresponding values for the hydrides with the same x (cf figures 2 and 3). For example, the $(T_1^{-1})_V^{\text{LTmax}}$ values for $\text{TaV}_2\text{D}_{0.84}$ and $\text{TaV}_2\text{H}_{0.87}$ are 335 and 120 s^{-1} , respectively. This means that the amplitude of electric-field-gradient (EFG) fluctuations at V sites in the deuterides is considerably higher than in the hydrides. Hence, the low- T isotope effects in H (D) motion in TaV_2 cannot be reduced to differences in frequency scales of the motion, and one has to assume that the effective 'amplitudes' of local motion of H and D atoms are different. The ^2D spin-lattice relaxation rates in TaV_2D_x are also found to exhibit double-peak temperature dependences, the ratios $(T_1^{-1})_D^{\text{LTmax}}/(T_1^{-1})_D^{\text{HTmax}}$ being considerably higher than $(T_1^{-1})_H^{\text{LTmax}}/(T_1^{-1})_H^{\text{HTmax}}$ for the corresponding hydrides. This is consistent with the ^{51}V relaxation data.

Phua *et al* (1983) have shown that the secondary low- T maxima in the temperature dependence of the ^1H spin-lattice relaxation rate may result from paramagnetic impurity effects related to the interplay of spin diffusion and hydrogen-atom diffusion. It should be stressed, however, that the frequency dependence of $(T_1^{-1})_H$ and the observation of low- T maxima for host-metal relaxation rates rule out the interpretation of our data in terms of such impurity effects. We can also exclude the possibility that the low- T

relaxation rate maxima originate from H (D) diffusion in the residual BCC phase since in this case the coexistence of broad and narrow ^1H NMR lines near 100 K and the non-exponential relaxation are expected but none of this behaviour is observed. Hence, we conclude that the low- T relaxation rate maximum is the intrinsic effect of H (D) motion in TaV_2 .

We now discuss the possible types of low-frequency local motion of H (D) atoms in TaV_2 . The first possibility is the H (D) hopping between two (or more) displaced sites within the tetrahedral interstitial. This mechanism may be related to some kind of H (D) ordering in displaced positions. In fact, according to the neutron diffraction data (Somenkov and Irodova 1984a, b) the D atoms in $\text{TaV}_2\text{D}_{1.6}$ are displaced by 0.1 Å from geometrical centres of g-interstitials. Our estimates show that the dynamical 0.1 Å displacements can account for the observed $(T_1^{-1})_{\text{H}}^{\text{L}^{\text{Tmax}}}$ values in TaV_2H_x . A similar mechanism of local motion was invoked to interpret the ^2D spin-relaxation data for LaD_3 (Borsa *et al* 1982). However, in the case of LaD_3 the double-peak temperature dependence of $(T_1^{-1})_{\text{D}}$ was not observed. The second possible mechanism is H (D) hopping between two tetrahedral g-interstitials with a common V–V–Ta face. In this case a H (D) nucleus is always bound to the same pair of nearest-neighbour V nuclei giving the dominant contribution to the rigid-lattice dipole–dipole interaction. This mechanism can also account for the observed $(T_1^{-1})_{\text{H}}^{\text{L}^{\text{Tmax}}}$ values for TaV_2H_x . In contrast to the dipole–dipole interaction responsible for ^1H spin relaxation, the quadrupole interaction of ^{51}V is not easily evaluated. Since the EFG values at V sites are expected to be very sensitive to V–H (D) distances, the strong difference between the values of $(T_1^{-1})_{\text{V}}^{\text{L}^{\text{Tmax}}}$ for the hydrides and the deuterides can be attributed to the difference between the displacements of the hydrogen isotopes. In the framework of the first model of local motion the experimental data on ^{51}V relaxation can be qualitatively explained if the displacement amplitude of D atoms is higher than that of H atoms. The explanation of the $(T_1^{-1})_{\text{V}}$ data in the framework of the second model requires a substantial difference between the equilibrium positions of H and D atoms in the g-interstitials.

While the detailed description of the local motion remains to be elucidated, it is clear that at $T = 100$ K the characteristic frequencies of the motion, $1/\tau_1$, are less than 10^9 s^{-1} , and the motion is not frozen on the NMR frequency scale even below 40 K. The observed strong isotope effects at low temperatures suggest a quantum origin of the local motion.

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