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LETTER TO THE EDITOR

## Localized motion of hydrogen in C15-type TaV<sub>2</sub>: a quasielastic neutron scattering study

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**Abstract.** In order to clarify the nature of the unusual low-temperature hydrogen motion in TaV<sub>2</sub>, we have performed high-resolution quasielastic neutron scattering measurements on TaV<sub>2</sub>H<sub>0.6</sub> in the temperature range 10–300 K. The results confirm the existence of localized H motion with the hopping rate of the order of 10<sup>9</sup> s<sup>-1</sup> at 90 K. The temperature dependence of the hopping rate appears to be non-Arrhenius. The behaviour of the elastic incoherent structure factor is consistent with the models of H jumps between three or six sites on a circle with radius  $r \approx 1.1$  Å.

The cubic C15-type intermetallic compound TaV<sub>2</sub> can absorb considerable amounts of hydrogen forming homogeneous solid solutions TaV<sub>2</sub>H<sub>*x*</sub> ( $x \leq 1.7$ ) [1]. For all *x* the single-phase state with the C15 host-lattice structure is retained down to 4 K. Recent nuclear magnetic resonance (NMR) measurements of <sup>1</sup>H, <sup>2</sup>D and <sup>51</sup>V spin–lattice relaxation rates in TaV<sub>2</sub>H<sub>*x*</sub> (D<sub>*x*</sub>) ( $0.22 \leq x \leq 1.54$ ) [2, 3] have revealed the anomalous localized H(D) motion which is not frozen out on the frequency scale 10<sup>7</sup>–10<sup>9</sup> s<sup>-1</sup> down to 30 K. This localized motion appears to be intrinsic (i.e. not related with hydrogen trapped by impurities or defects) and shows a number of unusual features including non-Arrhenius temperature dependence of the hopping rate and pronounced isotope effects [3]. The nature of this motion is not yet clear. The unusual H(D) dynamics in TaV<sub>2</sub>H<sub>*x*</sub> (D<sub>*x*</sub>) may be closely related with low-temperature hydrogen ordering proposed on the basis of the heat capacity measurements [4]. Such a relation has been found, for example, for α-YH<sub>*x*</sub> and α-ScH<sub>*x*</sub> [5] where both the anomalous H motion and the pronounced short-range order (pairing) are observed. In the present letter we report the results of high-resolution quasielastic neutron scattering (QENS) measurements for TaV<sub>2</sub>H<sub>0.6</sub> performed with the aim of clarifying microscopic details of the localized H motion.

The preparation of TaV<sub>2</sub>H<sub>0.6</sub> was analogous to that described in [2]. X-ray diffraction analysis has shown that the sample is a single-phase solid solution with the C15-type host-lattice structure and the lattice parameter  $a_0 = 7.22$  Å. QENS measurements were performed on the high-resolution backscattering spectrometer IN10 and the cold neutron time-of-flight spectrometer IN5 at the Institut Laue–Langevin in Grenoble. These two spectrometers complement each other with respect to the resolution and the accessible energy transfer range, giving the opportunity to probe hydrogen motion in the range of hopping frequencies 10<sup>8</sup>–10<sup>11</sup> s<sup>-1</sup>.

In the experiments on IN10, the Si(111) reflection was used in the monochromator and analysers resulting in the neutron wavelength of 6.271 Å. The range of energy transfer  $\hbar\omega$  was  $\pm 13.4 \mu\text{eV}$  with a resolution FWHM of about  $1 \mu\text{eV}$ . Eight analyser plates covered the range of momentum transfer  $\hbar Q$  corresponding to  $Q$  from 0.41 to  $1.94 \text{ \AA}^{-1}$ . The powdered  $\text{TaV}_2\text{H}_{0.6}$  sample was placed into a flat Al container with a depth of 1.1 mm. The plane of the container was oriented in the direction of the only Bragg reflection ( $2\theta \approx 98^\circ$ ) in the  $Q$ -range studied.

In the experiments on IN5, the incident neutron wavelength was 5.0 Å, the range of energy transfer was from  $-100 \text{ meV}$  to  $+2.42 \text{ meV}$  with a resolution FWHM of  $109 \mu\text{eV}$  and the elastic  $Q$ -range was from 0.09 to  $2.18 \text{ \AA}^{-1}$ . The sample was placed in the same container as for the measurements on IN10, the plane of the container being parallel to the line  $2\theta = 135^\circ$  (the highest-angle limit of the detector bank).

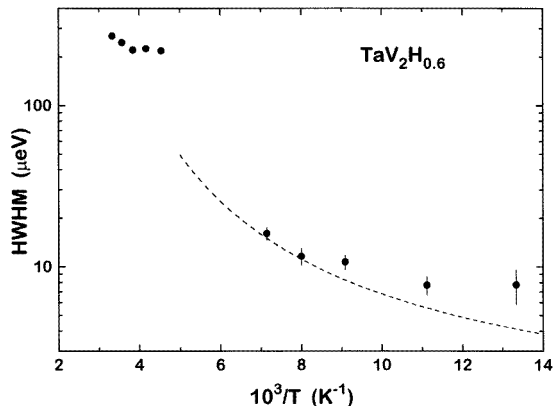
QENS spectra of  $\text{TaV}_2\text{H}_{0.6}$  were recorded at eight temperatures between 10 and 140 K on IN10 and at six temperatures (10 K and 220–300 K) on IN5. For both spectrometers the instrumental resolution function was determined from the measurements at 10 K. The background spectra were measured for the identical outgassed  $\text{TaV}_2$  sample at 140 K (IN10) and 220 K (IN5) in the same experimental geometry as for  $\text{TaV}_2\text{H}_{0.6}$ . The scattering function  $S_{\text{exp}}(Q, \omega)$  of the hydrogen sublattice was determined by subtracting these background spectra from the  $\text{TaV}_2\text{H}_{0.6}$  spectra.

As is typical of the case of localized motion, the corrected QENS spectra can be satisfactorily described by a sum of two components: a narrow ‘elastic’ line and a broader Lorentzian quasielastic line. More specifically, we have fitted  $S_{\text{exp}}(Q, \omega)$  measured on IN10 with the model scattering function

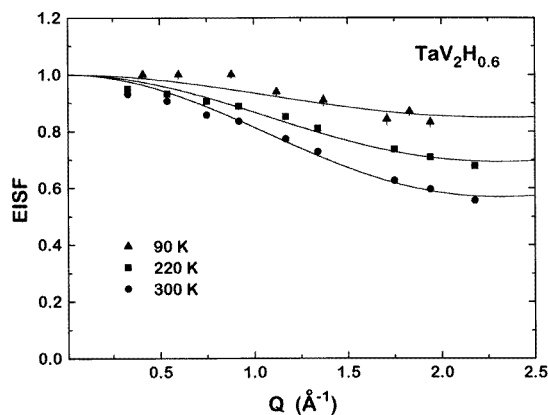
$$S(Q, \omega) = A_0(Q) \delta(\omega) + [1 - A_0(Q)]L(\omega) + B + C\omega \quad (1)$$

convoluted with the spectrometer resolution function. Here  $\delta(\omega)$  is the elastic  $\delta$ -function,  $L(\omega)$  is the quasielastic Lorentzian with the half-width  $\Gamma$ ,  $A_0(Q)$  is the elastic incoherent structure factor (EISF), and the terms  $B + C\omega$  represent the small sloping background. The value of  $\Gamma$  is proportional to the hydrogen hopping rate  $\nu$ , and  $A_0(Q)$  contains information on the geometry of localized motion [6]. For the high-temperature IN5 data the description is found to improve if  $\delta(\omega)$  in equation (1) is replaced by a Lorentzian  $L_0(\omega)$  with the half-width  $\Gamma_0$ . However, the fitted values of  $\Gamma_0$  (1 to  $9 \mu\text{eV}$ , depending on  $Q$  and  $T$ ) are much lower than both  $\Gamma$  and the IN5 resolution half-width. This small additional broadening of the ‘elastic’ component at high temperatures may result from jumps outside the regions of localized motion, i.e. from jumps leading to the long-range diffusion.

Below 75 K the quasielastic component has not been detected. At higher temperatures the half-width of this component  $\Gamma$  is found to be nearly  $Q$ -independent. Therefore, for the final assessment of parameters at each temperature we have used a simultaneous fit of  $S(Q, \omega)$  to the data at all  $Q$  with a common value of  $\Gamma$ . The temperature dependence of the fitted quasielastic half-width  $\Gamma$  is shown in figure 1. The corresponding  $\nu$ -values in the range 75–140 K are of the order of  $10^9$ – $2 \times 10^9 \text{ s}^{-1}$  being in general agreement with the NMR data [2, 3]. This means that the quasielastic line broadening observed in the present experiment originates from the same localized motion as that detected by NMR. As can be seen from figure 1, the observed temperature dependence of  $\Gamma$  is non-Arrhenius. The dashed line in figure 1 shows the behaviour of  $\nu$  (converted to units of  $\Gamma$ ), as estimated from the NMR measurements in  $\text{TaV}_2\text{H}_{0.56}$  in the range 70–200 K [3]. At low  $T$  this temperature dependence is also found to be much weaker than the Arrhenius one. Included in figure 1 are also representative high-temperature values of the ‘elastic’ half-width  $\Gamma_0$  at  $Q = 1.34 \text{ \AA}^{-1}$ .

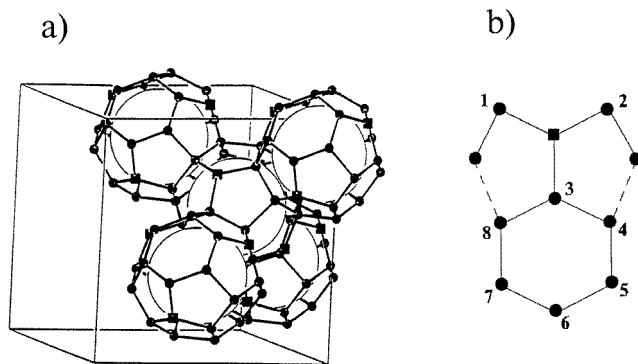


**Figure 1.** The half-width (HWHM) of the quasielastic Lorentzian line for  $\text{TaV}_2\text{H}_{0.6}$  measured on IN10 (solid triangles) and IN5 (solid circles) as a function of reciprocal temperature. The dashed line shows the behaviour of the H hopping rate (converted to units of  $\Gamma$ ), as estimated from the NMR measurements for  $\text{TaV}_2\text{H}_{0.56}$  [3]. Open circles show the 'elastic' half-width  $\Gamma_0$  obtained from the high-temperature IN5 data at  $Q = 1.34 \text{ \AA}^{-1}$ .

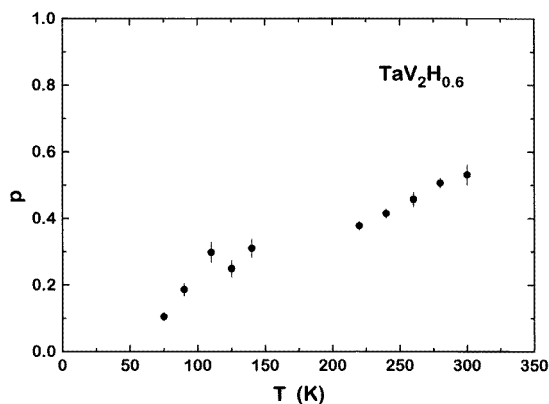


**Figure 2.** The elastic incoherent structure factor for  $\text{TaV}_2\text{H}_{0.6}$  as a function of  $Q$  at  $T = 90, 220$  and  $300 \text{ K}$ . The solid lines represent fits of the three-site model (equation (4)) with  $r = 1.13 \text{ \AA}$  to the data.

The behaviour of the elastic incoherent structure factor at three temperatures is shown in figure 2. Even for the highest  $Q$  accessible in the experiment the measured value of EISF appears to be above 0.5. Moreover, it shows pronounced temperature dependence, decreasing with increasing  $T$ . We now consider the possible geometrical models of the localized motion. According to the neutron diffraction data [7–9], D atoms in  $\text{TaV}_2\text{D}_x$  occupy only tetrahedral interstitial sites of g type ( $\text{Ta}_2\text{V}_2$ ), the other two types of tetrahedral site, e ( $\text{TaV}_3$ ) and b ( $\text{V}_4$ ), being empty. However, g sites in the C15 structure do not form any pairs (or other groups) well separated from the other sites. The spatial arrangement of g and e sites is shown schematically in figure 3(a). Each g site has four nearest neighbours: one e site and two g sites at a distance of  $0.152a_0$  and one g site at  $0.18a_0$ . For  $\text{TaV}_2\text{H}_{0.6}$  these distances are equal to 1.10 and 1.30  $\text{Å}$ , respectively. It has been suggested [3] that



**Figure 3.** The (a) Spatial arrangement of interstitial sites in the C15-type AB<sub>2</sub> compound (from [10]). Full squares: e sites; full circles: g sites; large open circles: A atoms. (b) A schematic representation of a part of the network of interstitial sites in TaV<sub>2</sub>. Solid and dashed lines represent the distances of about 1.1 Å and 1.3 Å, respectively. Models (iii) and (iv) correspond to jumps between sites 1–2–3 and 3–4–5–6–7–8, respectively.



**Figure 4.** The temperature dependence of the fraction of protons participating in the localized motion, as determined from fits of the three-site model (equation (4)) to the spectra measured on IN10 (triangles) and IN5 (circles).

the localized motion in TaV<sub>2</sub>H<sub>x</sub> may imply hopping of H atoms between two (or more) displaced sites within a tetrahedral interstitial. Our present QENS results allow us to exclude this possibility. In fact, for jumps between two sites separated by 0.5 Å the expected  $A_0$ -value at  $Q = 2.18 \text{ \AA}^{-1}$  is 0.907, whereas the observed  $A_0$ -values at  $T \geq 110 \text{ K}$  are considerably lower. This unambiguously shows that the localized H motion in TaV<sub>2</sub>H<sub>0.6</sub> is spatially more extended than the hopping within interstitial sites.

We have tried to fit four simple models of localized H motion to the data.

(i) Hopping between two equivalent sites. In order to describe the temperature dependence of EISF, we have to assume that only a fraction  $p$  of H atoms participate in the motion and that this fraction may change with temperature. In this case the form of

the EISF is

$$A_0(Q, T) = 1 - p(T) + \frac{1}{2}p(T)[1 + J_0(Ql)] \quad (2)$$

where  $J_0(x)$  is the Bessel function of zeroth order and  $l$  is the jump length. The fit at 300 K (corresponding to the widest range of  $A_0(Q)$ -variation) results in  $p = 0.71 \pm 0.04$ ,  $l = 1.95 \pm 0.12$  Å. This value of the jump length is considerably higher than the distance between the nearest-neighbour g sites. In fact, it corresponds to jumps to the third coordination sphere. Although such jumps can occur in Laves phase hydrides [11, 12], it is difficult to justify a formation of isolated *pairs* of sites with this  $l$ -value.

(ii) Hopping between two inequivalent sites. The formation of asymmetric double-well potentials with the asymmetry increasing with decreasing  $T$  may be expected for the system showing low- $T$  ordering of hydrogen. In this case all H atoms are assumed to participate in the motion, the temperature dependence resulting from changes in the ratio of back and forth hopping rates,  $\rho = \nu_1/\nu_2$ , due to the changing asymmetry. The form of the EISF is

$$A_0(Q, T) = \frac{1}{[1 + \rho(T)]^2} [1 + \rho^2(T) + 2\rho(T)J_0(Ql)]. \quad (3)$$

Although the physical origin of model (ii) differs from that of model (i), the form of  $A_0(Q, T)$  appears to be the same as in model (i) with  $4\rho/(1 + \rho)^2$  substituted for  $p$ . In particular, the fitted  $l$ -value is the same as for model (i). Therefore the above arguments against this model are also applicable here.

(iii) Hopping between three equivalent sites on a circle of radius  $r \approx 1.1$  Å with the temperature-dependent  $p$ . This model corresponds to H jumps between three g sites that are the nearest neighbours of one e site (see figure 3(b)). If the potential barriers for g–g jumps via intermediate e sites are lower than for direct g–g jumps, the motion of a hydrogen atom may be confined to the first coordination sphere of the e site. However, the localization of H in the e site itself can be excluded on the basis of the low-temperature neutron diffraction measurements [7, 9]. In this case

$$A_0(Q, T) = 1 - p(T) + \frac{1}{3}p(T)[1 + 2J_0(Qr\sqrt{3})]. \quad (4)$$

The fit of equation (4) to the data at 300 K with  $p$  and  $r$  as free parameters results in  $p = 0.53 \pm 0.03$ ,  $r = 1.13 \pm 0.07$  Å, i.e. the fitted value of  $r$  agrees perfectly with that taken from the crystal structure. By fixing the value of  $r$  to 1.13 Å, we have found reasonable fits of equation (4) to the data at all temperatures with  $p$  as the only fit parameter. The results of these fits are shown as solid lines in figure 2. The temperature dependence of the fitted  $p$ -value is shown in figure 4. The simplest model for describing  $p(T)$  is based on the assumption of a certain energy difference  $\Delta E$  between ‘static’ and ‘mobile’ H states (see, e.g., [5]). We have found, however, that such a model can only describe the observed temperature dependence of  $p(T)$  if there is a broad  $\Delta E$ -distribution. The details of this analysis will be presented elsewhere.

(iv) Hopping between six equivalent sites on a circle of radius  $r \approx 1.1$  Å with the temperature-dependent  $p$ . This model corresponds to H jumps between six g sites forming hexagons in  $\langle 111 \rangle$  directions (figure 3(a)). As can be seen from figure 3(b), the nearest-neighbour g–g distances for sites on the hexagon are 1.1 Å, being somewhat shorter than the distances between g sites on different hexagons (1.3 Å). This may result in the motion of H atoms confined to such hexagons. In this case

$$A_0(Q, T) = 1 - p(T) + \frac{1}{6}p(T)[1 + 2J_0(Qr) + 2J_0(Qr\sqrt{3}) + J_0(2Qr)]. \quad (5)$$

In the  $Q$ -range studied the behaviour of  $A_0(Q)$  for the six-site model is close to that for the three-site model (iii) with the same  $r$ . Strictly speaking, for the six-site model the quasielastic line should consist of three Lorentzian components with different half-widths and  $Q$ -dependent amplitudes [6]. Therefore the width of such a composite quasielastic line is expected to vary considerably with  $Q$ , especially at  $Qr \geq 1.5$  [6]. As noted above, the experimental half-width of the quasielastic component is found to be nearly  $Q$ -independent. Moreover, we have found that the inclusion of additional Lorentzian components relevant to the six-site model does not improve the quality of fits to the spectra. Thus the six-site model does not seem to be the preferable one. However, we cannot exclude the possibility that the absence of observable  $Q$ -dependence of the half-width of the quasielastic line may be due to the limited experimental accuracy. For instance, in the QENS study of hydrogen dynamics in  $\alpha$ -LaNi<sub>5</sub>H<sub>x</sub> [13] the broad quasielastic line is also found to be well described by a single Lorentzian with a  $Q$ -independent width, although there is practically no doubt that the localized H motion in this compound occurs over six-site rings.

In summary, our quasielastic neutron scattering measurements show the existence of fast localized motion of protons in TaV<sub>2</sub>H<sub>0.6</sub> with non-Arrhenius temperature dependence of the hopping rate. The preferable geometrical model of the motion is the model of H jumps between three equally spaced sites on a circle of radius  $r \approx 1.1$  Å. However, we cannot exclude the possibility that the model implying jumps between six sites on a circle of the same radius may be appropriate. In order to distinguish between these two models, it would be useful to study QENS spectra in the region of higher  $Q$  (2.2–4 Å<sup>-1</sup>).

The observed changes in EISF with temperature can be attributed to temperature-dependent fraction of protons participating in the localized motion,  $p(T)$ . It should be noted that in the analysis of the NMR data for TaV<sub>2</sub>H<sub>x</sub> (D<sub>x</sub>) [3] the possibility of  $p \neq 1$  was not considered. The present QENS results suggest a plausible explanation of the strong effect of isotope (H  $\leftrightarrow$  D) substitution on the <sup>51</sup>V spin-lattice relaxation rate induced by the localized H(D) motion in TaV<sub>2</sub>H<sub>x</sub> (D<sub>x</sub>) [2, 3]. In particular, the mean square values of electric-field-gradient fluctuations at V sites in TaV<sub>2</sub>D<sub>x</sub> are found to be considerably higher than in TaV<sub>2</sub>H<sub>x</sub> with the same  $x$ . This feature may be naturally explained if we assume that the value of  $p$  for D is higher than for H because of the lower energy of excitation to a mobile state for deuterium.

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