Localized hydrogen motion in C15-type TaV$_2$H$_{0.65}$: temperature dependence of the H jump rate

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Abstract

In order to study the temperature dependence of the jump rate τ_l^{-1} for the fast localized motion of hydrogen in cubic (C15-type) Laves-phase TaV$_2$, we have performed time-of-flight quasielastic neutron scattering measurements for TaV$_2$H$_{0.65}$ over the temperature range 12–290 K. The quasielastic line broadening corresponding to the localized H motion has been observed down to 70 K; the observability of the quasielastic line at lower temperatures is limited by the decrease in the fraction of H atoms participating in the fast localized motion. In the range 70–290 K the temperature dependence of τ_l^{-1} is found to deviate from the Arrhenius behaviour. This temperature dependence can be reasonably well described by the exponential function $\exp(T/T_0)$ with $T_0 = 220$ K. The same function with T_0 of the order of 100 K also appears to describe $\tau_l^{-1}(T)$ in some other metallic systems showing fast localized hydrogen motion.

1. Introduction

One of the interesting features of hydrogen diffusion in cubic (C15-type) Laves-phase intermetallic compounds is a coexistence of two H jump processes with different characteristic jump rates [1–6]. For most of the C15-type hydrides AB$_2$H$_x$ studied where hydrogen atoms occupy only tetrahedral sites of g type (A$_2$B$_2$), the faster process corresponds to localized H motion within the hexagons formed by g sites, and the slower process is associated with H jumps from one g-site hexagon to another. The difference between the characteristic frequencies of these jump processes is believed to originate from the difference between the g–g distances r_1 (within the hexagons) and r_2 (between the nearest hexagons). For C15-type compounds TaV$_2$H$_x$ the value $r_2/r_1 = 1.45$ is the highest among the cubic Laves-phase hydrides studied [5]; therefore, these compounds show the highest ratio of the H jump rates for the two processes. For example, for TaV$_2$H$_{1.1}$ this ratio is found to be about 6×10^3 at room temperature [5].

The localized H motion in TaV$_2$H$_x$ is extremely fast. As follows from the nuclear magnetic resonance (NMR) measurements of the proton spin–lattice relaxation rates [2], in TaV$_2$H$_x$ with $x < 1$ the localized H motion is not 'frozen

out' on the frequency scale of 10^8 s^{-1} down to 20 K. The ultrasonic experiments on TaV$_2$H$_x$ with small x [7] have shown that the jump rate of a certain fraction of H atoms remains well above the ultrasound frequency ($\sim$1 MHz) down to 0.3 K. NMR [2, 8] and ultrasonic attenuation [7, 9] data suggest that the temperature dependence of the jump rate τ_l^{-1} for the localized H (D) motion in TaV$_2$H$_x$ (TaV$_2$D$_x$) is strongly non-Arrhenius. In particular, the temperature dependence of τ_l^{-1} derived from the NMR data [2, 8] in the range 20–200 K can be reasonably well described by the exponential function

$$\tau_l^{-1} = \tau_{l0}^{-1} \exp(T/T_0) \tag{1}$$

with T_0 of the order of 100 K. This unusual dependence is much weaker than the Arrhenius one at low temperatures. Although the relation given by equation (1) should be considered as empirical, it is worth noting that a similar term in the jump rate has been found in the framework of the quantum diffusion theory taking into account the effects of barrier fluctuations [10, 11]. Unfortunately, the behaviour of $\tau_l^{-1}(T)$ obtained from both the proton NMR and ultrasonic attenuation data may be affected by the temperature dependence of the fraction p of H atoms participating in the fast localized

motion [3]. The existence of a fraction $1 - p$ of 'static' H atoms is expected to originate from the H–H interaction leading to the formation of some ordered atomic configurations at low temperatures. As the temperature increases, such ordered configurations are progressively destroyed by thermal fluctuations; this results in the growth of p with increasing T. Since both the measured proton spin–lattice relaxation rate and the ultrasonic attenuation should be proportional to p [3], it is difficult to distinguish between the changes in these quantities caused by $\tau_l^{-1}(T)$ and $p(T)$. On the other hand, measurements of the quasielastic neutron scattering (QENS) spectra, in principle, allow one to determine τ_l^{-1} and p independently, the former from the linewidth of the quasielastic component and the latter from the elastic incoherent structure factor [12, 13].

Previous QENS studies of TaV$_2$H$_x$ [3, 14] were focused mainly on elucidation of the geometry of the localized H motion; the temperature dependence of τ_l^{-1} has not been studied in detail. It should be noted that QENS measurements using the neutron backscattering technique [12, 13] have a very narrow range of the energy transfer (or in other words, a narrow frequency 'window'). Because of this, such measurements are hardly suitable for tracing the temperature dependence of τ_l^{-1} over a wide T range, especially in cases where a certain distribution of τ_l^{-1} values is possible. The time-of-flight QENS technique [12, 13] having a wide range of energy transfer seems to be preferable. Previous time-of-flight QENS measurements for TaV$_2$H$_x$ [3, 14] were performed only in the temperature range 200–300 K. In order to study non-Arrhenius temperature dependence of τ_l^{-1} and, in particular, to verify the relation given by equation (1), it is crucial to measure the quasielastic linewidth at lower temperatures. At a given temperature, the hydrogen jump rate τ_l^{-1} in TaV$_2$H$_x$ (TaV$_2$D$_x$) is known to increase with decreasing H (D) content [2, 3]; therefore, samples with low x should be more suitable for low temperature QENS studies. In the present work, we report the results of time-of-flight QENS measurements for TaV$_2$H$_{0.65}$ over the temperature range 70–290 K. The hydrogen concentration in this sample has been chosen as a compromise between the high H jump rates and the scattered neutron intensity (which decreases with decreasing H content).

2. Experimental details

The intermetallic compound TaV$_2$ was prepared by arc melting the appropriate amounts of high purity Ta and V in a helium atmosphere followed by an annealing in vacuum at 950 °C for 100 h. According to x-ray diffraction analysis, the annealed sample was a single-phase compound with the cubic C15-type structure and the lattice parameter $a = 7.159$ Å. Small pieces of TaV$_2$ were hydrogenated at a pressure of about 1 bar using a Sieverts-type vacuum system. After annealing the intermetallic in vacuum at 700 °C, H$_2$ gas was admitted into the system at this temperature. The amount of absorbed hydrogen (0.65 ± 0.05 H atoms per formula unit) was determined from the pressure change in the calibrated volume of the system after slowly cooling down to room temperature. The resulting TaV$_2$H$_{0.65}$ sample was found to be a single-phase compound

with the C15-type host lattice and the lattice parameter $a = 7.224$ Å.

QENS measurements were performed on the disc-chopper time-of-flight spectrometer IN5 at the Institute Laue-Langevin (ILL) in Grenoble. In addition to having a well-defined instrumental resolution function without long 'wings', this spectrometer allows one to optimize experimental conditions by changing the incident neutron wavelength λ, the energy resolution and the neutron-beam intensity. In order to extend the temperature range in which useful information could be extracted from QENS spectra, measurements were made with two values of λ, 5 Å and 8 Å. In the case of $\lambda = 5$ Å with the chopper speed of 8500 revolutions per minute, the energy resolution was 109 μeV (full width at half-maximum) and the maximum value of the elastic momentum transfer $\hbar Q$ corresponded to $Q_{\max} = 2.24$ Å^{-1}. In the case of $\lambda = 8$ Å with the same chopper speed, the energy resolution was 28 μeV and $Q_{\max} = 1.40$ Å^{-1}. QENS measurements using these two experimental configurations complement each other, the former having the advantage of high neutron intensity and broader range of Q, and the latter having high energy resolution. QENS spectra $S(Q, \omega)$, where $\hbar\omega$ is the energy transfer, were measured in the temperature ranges 125–290 K ($\lambda = 5$ Å) and 70–190 K ($\lambda = 8$ Å). The powdered TaV$_2$H$_{0.65}$ sample was placed into a flat Al container, the sample thickness being 0.5 mm. The sample thickness was chosen to ensure $\sim$90% neutron transmission and thus minimize multiple-scattering effects. The plane of the container was oriented along the line $2\theta = 135°$ (the highest angle limit of the detector bank). For data analysis, the detectors were binned into nine groups. The scattering angles corresponding to the Bragg reflections were excluded from the analysis. The raw experimental data were corrected for absorption and self-shielding using the standard ILL programs. The instrumental resolution functions were determined from the measured QENS spectra of TaV$_2$H$_{0.65}$ at 12 K.

3. Results and discussion

At $T \geqslant 70$ K the experimental QENS spectra can be satisfactorily described by a sum of two components: a narrow 'elastic' line represented by the spectrometer resolution function $R(Q, \omega)$ and a resolution-broadened Lorentzian 'quasielastic' line. As an example of the data, figure 1 shows the QENS spectrum for $\lambda = 8$ Å and $Q = 0.73$ Å^{-1} measured at 170 K. As the first step of the analysis, we have fitted the measured spectra with the model incoherent scattering function

$$S_{\text{inc}}(Q, \omega) = A_0(Q)\delta(\omega) + [1 - A_0(Q)]L(\omega, \Gamma) \quad (2)$$

convoluted with $R(Q, \omega)$. Here $\delta(\omega)$ is the 'elastic' δ-function, $L(\omega, \Gamma)$ is the 'quasielastic' Lorentzian function with the half-width Γ and A_0 is the elastic incoherent structure factor (EISF). An example of the fit based on equation (2) is shown in figure 1. At all the temperatures studied, the relative intensity of the 'quasielastic' component is found to increase with increasing Q, its half-width Γ being nearly independent of Q. These features are typical of the case of spatially confined (localized)
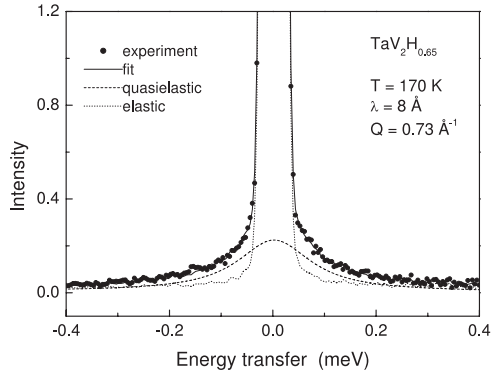
Figure 1. The QENS spectrum for $TaV_2H_{0.65}$ measured at $T = 170$ K, $\lambda = 8$ Å and $Q = 0.73$ Å^{-1}. The full curve shows the fit of the two-component model (equation (2)) to the data. The dotted curve represents the elastic component (the spectrometer resolution function), and the dashed curve shows the Lorentzian quasielastic component.

Figure 2. The temperature dependence of the fraction of H atoms participating in the fast localized motion, as determined from the fits of the six-site model (equations (4)–(7) and (3)) to the QENS spectra for $TaV_2H_{0.65}$. The full curve shows the fit of equations (8) and (9) to the $p(T)$ data.

motion [12, 13]. The value of Γ is proportional to the hydrogen jump rate τ_l^{-1}, and $A_0(Q)$ contains information on the geometry of the localized motion [12, 13].

The spatial aspects of the localized H motion in TaV_2H_x have been discussed in detail in our previous papers [3, 5, 14]. It has been found that this motion corresponds to H jumps within the regular g-site hexagons. The distance r_1 between the nearest-neighbour g sites within the hexagons can be obtained from the structural data. Using the positional parameters of D atoms at g sites in TaV_2D_x ($X_g = 0.055$, $Z_g = 0.888$) [15] and the actual lattice parameter for $TaV_2H_{0.65}$, we obtain $r_1 = 0.98$ Å. Taking into account that only a fraction p of the H atoms participate in the fast localized motion [3], the elastic incoherent structure factor for the six-site model [12] can be written as

$$A_0(Q) = 1 - p + \frac{p}{6}[1 + 2j_0(Qr_1) + 2j_0(Qr_1\sqrt{3}) + j_0(2Qr_1)], \quad (3)$$

where $j_0(x)$ is the spherical Bessel function of zeroth order. We have verified that the model based on equations (2) and (3) with the fixed $r_1 = 0.98$ Å gives a reasonable description of the experimental QENS spectra at $T \geqslant 70$ K for both values of λ and all values of Q studied.

However, a more rigorous description of the quasielastic component for the six-site localized motion requires three Lorentzian lines with Q-dependent amplitudes [12],

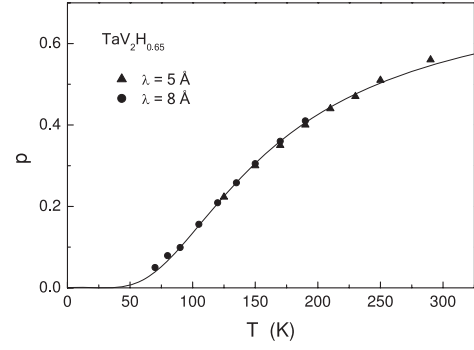$$S_{inc}(Q, \omega) = A_0(Q)\delta(\omega) + p \sum_{i=1}^{3} A_i(Q)L(\omega, \Gamma_i), \quad (4)$$

where $A_0(Q)$ is given by equation (3), and

$$A_1(Q) = \frac{1}{6}[2 + 2j_0(Qr_1) - 2j_0(Qr_1\sqrt{3}) - 2j_0(2Qr_1)], \quad (5)$$

$$A_2(Q) = \frac{1}{6}[2 - 2j_0(Qr_1) - 2j_0(Qr_1\sqrt{3}) + 2j_0(2Qr_1)], \quad (6)$$

$$A_3(Q) = \frac{1}{6}[1 - 2j_0(Qr_1) + 2j_0(Qr_1\sqrt{3}) - j_0(2Qr_1)]. \quad (7)$$

Here $L(\omega, \Gamma_i)$ is the Lorentzian function with the half-width Γ_i, $\Gamma_1 = 0.5\tau_l^{-1}$, $\Gamma_2 = 1.5\tau_l^{-1}$, $\Gamma_3 = 2\tau_l^{-1}$, and τ_l is the

mean time between two successive jumps of a hydrogen atom within a hexagon. As the next step of the data analysis, we have used the approach based on a simultaneous fit of the six-site model (equations (4)–(7) and (3)) with the fixed $r_1 = 0.98$ Å to the QENS spectra at all Q. For each of the temperatures studied, there are only two fit parameters (τ_l^{-1} and p) for nine QENS spectra corresponding to different Q values. The fits have been corrected for a contribution of the host-metal nuclei to the intensity of the elastic line ($\sim$17%, as estimated from the corresponding scattering cross-sections). The quality of the fits for individual QENS spectra is comparable to that for the simplified model with one Lorentzian and a delta function.

The temperature dependences of p and τ_l^{-1} resulting from the fits are shown in figures 2 and 3. As can be seen from figure 2, below 150 K the fraction of H atoms participating in the fast localized motion decreases rapidly with decreasing temperature. It is this drop of p that limits the observability of the quasielastic line at low temperatures; the width of the quasielastic line remains well above the energy resolution even at 70 K. In the range 170–250 K, the behaviour of $p(T)$ can be roughly described by the linear function cT, as reported earlier [3]. The usual approach to the description of $p(T)$ is based on the assumption of a certain energy gap ΔE between the 'static' and 'mobile' H states (see, e.g., [16]). In this case,

$$p(T) = \frac{b(T)}{1 + b(T)}, \quad (8)$$

$$b(T) = b_m \exp(-\Delta E / k_B T), \quad (9)$$

where b_m is the relative degeneracy factor of 'mobile' states. The solid curve in figure 2 shows the fit of this model to the $p(T)$ data; the corresponding fit parameters are $\Delta E = 26.9 \pm 0.4$ meV and $b_m = 3.5 \pm 0.1$.

As can be seen from figure 3, the observed temperature dependence of τ_l^{-1} in the range 70–290 K strongly deviates from the Arrhenius behaviour. The Arrhenius fits to the data in the ranges 210–290 and 70–120 K (dotted and dashed lines in figure 3) yield the apparent activation energies of 24 and 3 meV, respectively. A similar break in the Arrhenius plot of the jump rate for the localized H motion has been reported by
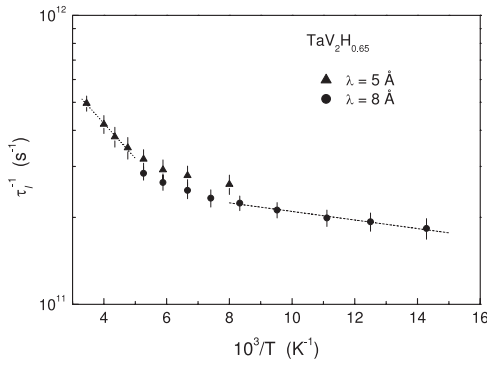
Figure 3. The hydrogen jump rates (resulting from the fits of the six-site model to the QENS spectra) as functions of the inverse temperature. The dotted and dashed lines show the Arrhenius fits to the data in the ranges 210–290 K and 70–120 K, respectively.
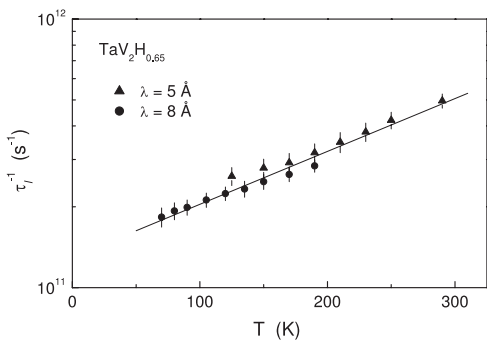
Figure 4. The data of figure 3 replotted as lg τ_l^{-1} versus T. The full line shows the fit of equation (1) to all the experimental data.

Bull *et al* [17] for C15-type $ZrV_2H_{1.1}$ in the range 240–525 K. Figure 4 shows the data of figure 3 replotted as lg τ_l^{-1} versus T. It can be seen that the resulting plot is close to the linear one, i.e. the temperature dependence of τ_l^{-1} is reasonably well described by the exponential law (equation (1)). The solid line in figure 4 shows the fit of equation (1) to all the experimental data; the corresponding fit parameters are $T_0 = 220 \pm 14$ K and $\tau_{l0}^{-1} = (1.30 \pm 0.06) \times 10^{11}$ s^{-1}.

Inspection of the experimental results for systems with the fast localized hydrogen motion suggests that the applicability of equation (1) is not restricted to hydrogen in Laves-phase TaV_2–H (D). In particular, this equation appears to describe the behaviour of $\tau_l^{-1}(T)$ for the trapped hydrogen in $Nb(OH)_{0.011}$ [18] in the range 100–300 K and for 'mobile' H atoms in α-$ScH_{0.16}$ [19] in the range 125–300 K. The corresponding data and the fits based on equation (1) are shown in figure 5; the values of the fit parameters are $T_0 = 131$ K and $\tau_{l0}^{-1} = 2.9 \times 10^{10}$ s^{-1} for $Nb(OH)_{0.011}$ and $T_0 = 146$ K and $\tau_{l0}^{-1} = 1.0 \times 10^{10}$ s^{-1} for α-$ScH_{0.16}$. It should be noted that the authors [18, 19] have not analysed their data in terms of equation (1). As mentioned above, the temperature dependence of the type described by equation (1) has been predicted by the quantum diffusion theory [10, 11]. More precisely, the jump rate for the process of phonon-assisted incoherent tunnelling is found [10, 11] to be proportional to $\exp(-E/k_BT + T/T_0)$. Both terms in the exponent correspond to the increase in the
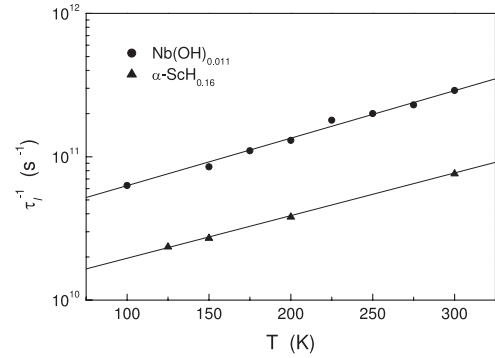
Figure 5. The temperature dependences of the jump rates for the localized hydrogen motion in $Nb(OH)_{0.011}$ [18] and α-$ScH_{0.16}$ [19]. The full lines show the fits of equation (1) to the data.

jump rate with increasing temperature. The first term is due to the small polaron effect [20]; in contrast to the classical case, the value of E here is not determined by the height of a potential barrier. The second term in the exponent originates from the effect of barrier fluctuations which facilitate the tunnelling [10, 11]. The value of T_0 is related to a susceptibility of the barrier height to certain displacements of host-metal atoms. Our results suggest that the behaviour of τ_l^{-1} in TaV_2H_x (and in a number of other metallic systems) may be governed by the effect of barrier fluctuations over a rather wide temperature range.

4. Conclusions

The analysis of our quasielastic neutron scattering data for C15-type $TaV_2H_{0.65}$ has shown that the hydrogen jump rate τ_l^{-1} for the fast localized motion in this system strongly deviates from the Arrhenius behaviour in the temperature range studied, 70–290 K. The temperature dependence of τ_l^{-1} in this range can be reasonably well described by the exponential function $\exp(T/T_0)$ with $T_0 = 220$ K. At 70 K the value of τ_l^{-1} remains well above the width of the instrumental resolution function, and the observability of the localized H motion using time-of-flight QENS at lower temperatures is limited by the drop of the fraction of H atoms participating in the motion (on the corresponding frequency scale). We have also found that the exponential function $\exp(T/T_0)$ with T_0 of the order of 100 K can describe the temperature dependences of the jump rates for the trapped hydrogen in $Nb(OH)_{0.011}$ [18] and for 'mobile' H atoms in α-$ScH_{0.16}$ [19] in the range ∼100–300 K.

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