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$\mathrm{TaV_2H(D)}_x$

An ultrasonic study of hydrogen (deuterium) motion in the C-15 Laves-phase compound $TaV_2H(D)_x$

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Abstract. Ultrasonic measurements have been carried out on $TaV_2H(D)_x$ over the temperature range of 15–335 K. Temperature-dependent attenuation peaks were observed with maxima near 250 K for measurement frequencies near 1 MHz. These peaks are believed to be due to the same process as responsible for maxima in NMR spin–lattice relaxation rates observed at higher frequencies and temperatures, and associated with long-range hydrogen diffusion. The present results for activation energies and attempt frequencies are in agreement with the NMR results in the temperature range of the spin–lattice relaxation rate measurements, but the ultrasonic data suggest the presence of two Arrhenius processes for the long-range motion below about 200 K. The most significant result of the present measurements concerns a possible second peak at low temperatures associated with the local motion found in NMR and neutron measurements. For the present results, such a peak was *not* found in TaV_2H_x, but there was an indication of such a peak in TaV_2D_x for temperatures below 50 K. These results suggest that the H hopping rate for the local motion in $TaV_2H(D)_x$ remains well above the ultrasonic frequencies used throughout the temperature range of the measurements, but that the D hopping rate is somewhat lower.

1. Introduction

The motion of hydrogen in metals is of great interest for both technological and scientific reasons [1]. The technological interest stems from the use of metals for hydrogen storage, and other applications. The scientific interest arises from the rich variety of diffusion mechanisms related to the interactions of these light interstitials with phonons and conduction electrons. Laves-phase materials—intermetallic AB_2 compounds—have received much study in recent years [2–6] due to their ability to absorb relatively large amounts of hydrogen. The motion of hydrogen in these materials tends to be more complex than in pure metals due to the large number and variety of interstices. Both nuclear magnetic resonance (NMR) and neutron scattering experiments on the cubic C-15 intermetallic compound $TaV_2H(D)_x$ indicate unusual motion [7–10]. The NMR spin–lattice relaxation rates show two maxima as a function of temperature. The high-temperature peak is associated with long-range diffusion, while the low-temperature peak is attributed to a localized motion of the hydrogen. Quasielastic neutron scattering measurements confirm the rapid, localized motion. There are three types of interstitial site in C-15 compounds, all with a tetrahedral coordination. Per formula unit AB_2 there are 12 g sites (surrounded by two A atoms and two B atoms), four e sites (surrounded by one A atom and three B atoms) and one b site (surrounded by four B atoms). The b site is too small to contain hydrogen. Hydrogen only occupies the g site [11, 12] in TaV_2. The unusual, rapid localized motion has been attributed to two possibilities: hopping of H among

three g sites which are nearest neighbours to an e site or hopping among six g sites which form a hexagon, the plane of the hexagon being perpendicular to the $\langle 111 \rangle$ directions. More recent evidence supports the six-site model [10]. Long-range H diffusion appears to occur by hopping between adjacent hexagons [10].

The rare-earth metals also exhibit at least two types of motion: one type leads to long-range diffusion; the second type appears to be localized. The rapid localized motion persists to low temperatures. In addition to being observed by NMR and neutron experiments, the low temperature motion in ScH_x, ScD_x and YD_x was observed by ultrasonic attenuation measurements [13, 14]. Ultrasound measurements provide a nice complement to NMR and neutron measurements for the study of hydrogen motion. With ultrasound it is possible to investigate time scales which are difficult or impossible with the other techniques. In addition, ultrasound couples to the hydrogen motion differently than the other techniques which can be a source of additional information. There have been few reports of the use of ultrasound to study hydrogen motion in intermetallic compounds, although hydrogen hopping in C-16 type materials has been studied experimentally and theoretically [15, 16]. It appears that such work has not been carried out on C-15 materials. Based on these considerations we decided to carry out ultrasonic measurements on $TaV_2H(D)_x$.

2. Experimental details

Polycrystalline ingots of the TaV_2 compounds were prepared as described previously [7]. X-ray measurements indicate that the single phase C-15 structure is retained down to 4 K. Ultrasonic measurements were made on samples of $TaV_2H_{0.34}$, $TaV_2H_{0.53}$ and $TaV_2D_{0.17}$. Samples in the approximate shape of rectangular parallelepipeds, about 2 mm on an edge, were cut from the ingots using a low-speed diamond saw. These saw-cut pieces were then polished into rectangular parallelepipeds for the ultrasonic measurements. The measurements were made using the technique of resonant ultrasound spectroscopy [17–19]. With this technique a sample is placed corner to corner between two piezoelectric transducers. Using one transducer for excitation and one for detection, a large number of the lowest-frequency vibrational eigenmodes of the parallelepiped are investigated. In the present study the frequencies and Q values of these eigenmodes were measured as a function of temperature. The Q is defined in the usual way as $f_0/\Delta f$ where f_0 is the resonant frequency of a particular eigenmode and Δf is the full width of the resonance at the half-power points. It is common practice to express the ultrasonic loss as $1/Q$. The temperature was controlled using an electronic controller with heater and a gas flow cryostat.

3. Results and discussion

Figure 1 shows ultrasonic loss results for $TaV_2H_{0.34}$ at frequencies of 0.500 and 0.750 MHz over the temperature range of 15–325 K. Figure 2 shows similar results for $TaV_2H_{0.53}$ measured at the frequencies of 0.645, 0.872 and 1.340 MHz. Figure 3 shows loss data for $TaV_2D_{0.17}$ over the temperature range of 120–330 K. These figures show no indication of a second peak at lower temperature as was found for NMR spin–lattice relaxation rates. Although the initial measurements on $TaV_2D_{0.17}$ were not extended below 120 K, it was decided to make such measurements in order to search for a low-temperature peak in this material as well. Figure 4 presents the results in an expanded view of the low-temperature region for $TaV_2D_{0.17}$. Results for $TaV_2H_{0.53}$ and TaV_2 are also presented. Figure 4 clearly shows a difference for $TaV_2D_{0.17}$ as compared to the other materials; the attenuation in $TaV_2D_{0.17}$ increases with decreasing

Figure 1. Ultrasonic loss data against temperature for $TaV_2H_{0.34}$. The filled and open symbols represent the data, and the solid lines are theoretical fits to the data using the parameters of table 1.
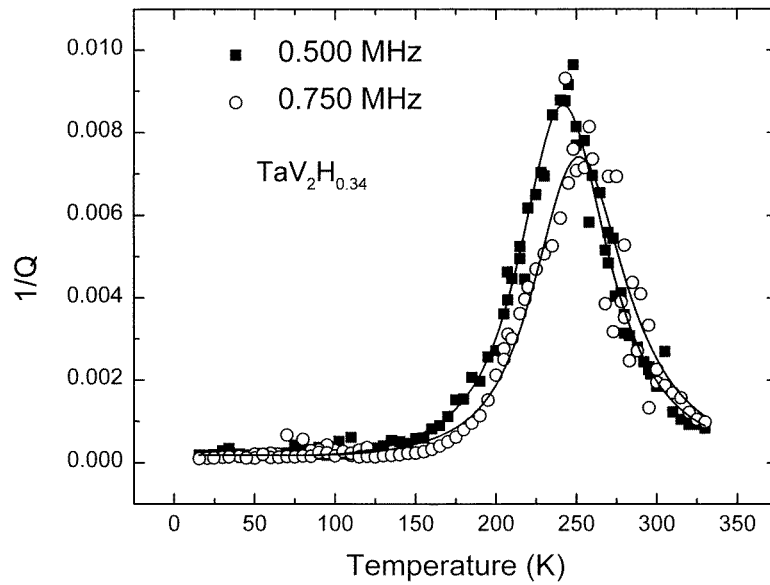

Figure 2. Ultrasonic loss data against temperature for $TaV_2H_{0.53}$. The filled and open symbols represent the data, and the solid lines are theoretical fits to the data using the parameters of table 1.
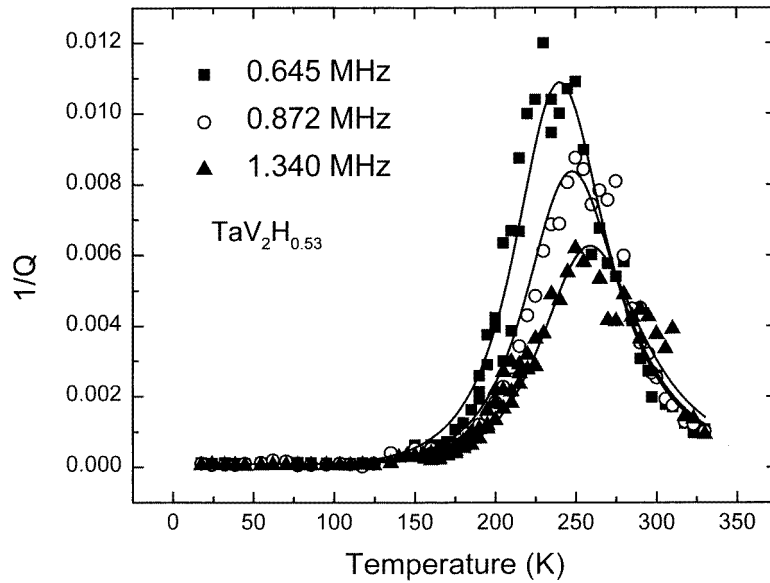
temperatures. We measured $1/Q$ in $TaV_2D_{0.17}$ for six different frequencies in the range 0.9–3.7 MHz; similar measurements were performed on TaV_2, $TaV_2H_{0.34}$ and $TaV_2H_{0.54}$. All measurements on $TaV_2D_{0.17}$ showed the increasing attenuation toward lower temperatures, but this feature was not observed in the other materials for any frequency.
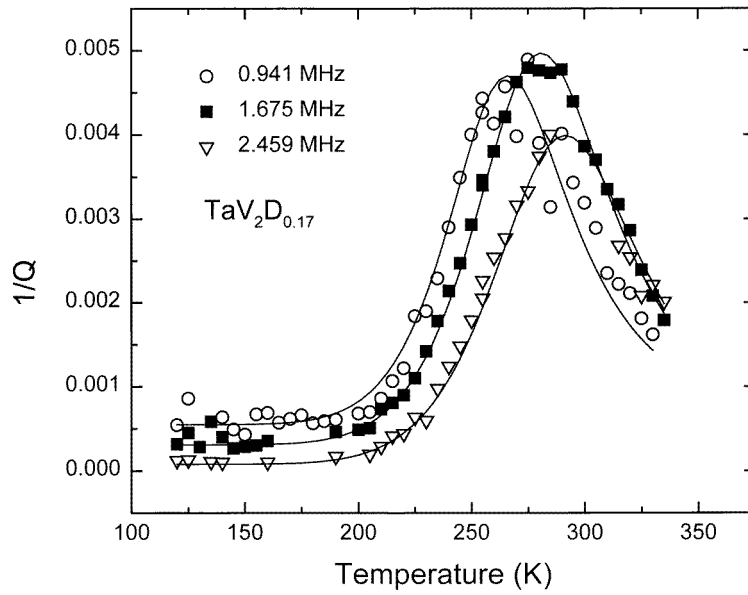
Figure 3. Ultrasonic loss data against temperature for $TaV_2D_{0.17}$. The filled and open symbols represent the data, and the solid lines are theoretical fits to the data using the parameters of table 1.
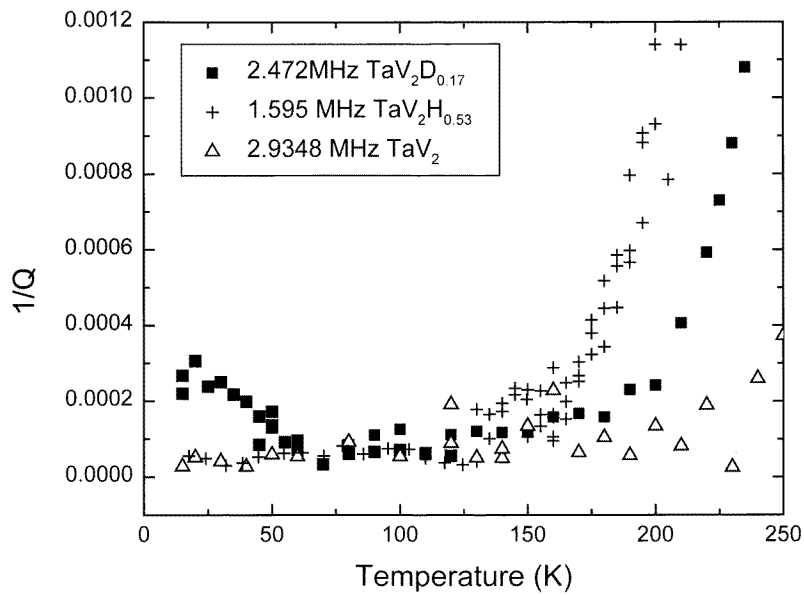
Figure 4. Expanded view of the ultrasonic loss against temperature for the lower temperatures. Data are presented for TaV_2, $TaV_2H_{0.53}$ and $TaV_2D_{0.17}$.

We interpret the high-temperature attenuation peaks as a Debye-type relaxation involving hydrogen hopping between two nearby interstitial sites. An interstitial atom such as hydrogen, which may occupy either of two nearby interstitial sites, can be described as a two-level system

with an energy splitting $\Delta E = 2(E_T^2 + A^2)^{1/2}$ where $2E_T$ is the tunnel splitting and $2A$ is the difference in site energy (asymmetry). The ultrasonic loss $1/Q$ due to relaxation is given by [20–22]

$$\frac{1}{Q} = \frac{nD^2}{k_B T C} \frac{\omega \tau_R}{1 + \omega^2 \tau_R^2} \tag{1}$$

where n is the concentration of hydrogen atoms contributing to the attenuation, $D = \partial(\Delta E)/\partial \varepsilon$ is the variation of the energy level splitting with respect to the ultrasonic strain ε, C is an elastic constant, $\omega/2\pi$ is the ultrasonic frequency and τ_R is the relaxation time. In the classical case tunnelling is not a factor and $E_T = 0$. In writing (1) it is assumed that $\Delta E \ll k_B T$. The data seem to be described by this assumption. If that is not the case then there is an additional factor of $\text{sech}^2[\Delta E/k_B T]$ multiplying the right-hand side of (1). It is usually assumed that the ultrasonic strain modulation of ΔE is due to a modulation of A, not E_T. Thus, relaxation attenuation will only occur if the two sites involved are nonequivalent with respect to the applied stress. As mentioned above, hydrogen occupies the g site in TaV₂. Each Ta atom is surrounded by 24 g sites and four e sites forming an arrangement of four hexagons and 12 pentagons. Each g site sits on one and only one hexagon. According to the selection rules for anelasticity [23], anelastic relaxation is possible if the defect symmetry is lower than the crystal symmetry. Such is the case for a defect atom on the g site. Thus, symmetry permits a non-zero D for relaxation involving nearby g sites. The temperature at which the attenuation peaks occur indicate that they are the same peaks as observed by NMR experiments [7, 8]. We assume that the relaxation time τ_R is approximately that of the mean dwell time of hydrogen in an interstitial site [24], although the relaxation time involved in the ultrasonic measurements may not be exactly the same as that involved in the spin–lattice relaxation measurements [25].

Guided by the NMR results we attempted to fit the data using an Arrhenius expression for τ_R,

$$\tau_R = \tau_{R_0} \exp(E_a/k_B T) \tag{2}$$

where $1/\tau_{R_0}$ is an attempt frequency and E_a is an activation energy. The data were fitted reasonably well by this approach with activation energies and attempt times as given in table 1; however, these energies are somewhat lower than the 0.23–0.24 eV found by Skripov *et al* [8] from NMR spin–lattice relaxation time measurements in TaV₂Hₓ for comparable concentrations. The NMR measurements were carried out at considerably higher frequencies (19.3–90 MHz) than were the present measurements. As a consequence, the peaks in the relaxation rates occurred at higher temperatures. Renz *et al* [3] found strong deviations from a simple Arrhenius law for the diffusion in the related Laves-phase system ZrCr₂Hₓ below about 180 K. They were able to give a satisfactory description of the diffusion as a sum of two Arrhenius terms. Motivated by these considerations, we assume that the relaxation rate is due to the sum of two rates

$$\tau_R^{-1} = \tau_1^{-1} + \tau_2^{-1} \tag{3}$$

where

$$\tau_i = \tau_{0i} \exp(E_i/k_B T) \tag{4}$$

with $i = 1, 2$. The solid lines in figures 1 and 2 are the result of fitting equations (1), (3) and (4) to the data. A temperature-independent background term was also included. The fitting parameters are given in table 1. For TaV₂D₀.₁₇ there was no indication of a second component to the relaxation at low temperatures, and (2) was used for the relaxation time. The rate τ_1^{-1} dominates at higher temperatures while the rate τ_2^{-1} dominates at lower temperatures. For both TaV₂H₀.₃₄ and TaV₂H₀.₅₃, $\tau_1^{-1} = \tau_2^{-1}$ at $T \approx 200$ K; this explains why the present results

Table 1. Fitting parameters for the solid curves in figures 1–3. E_a and τ_0 are the parameters used for a single Arrhenius process. Curves using these two parameters are shown only in figure 3. E_{a1}, τ_{01}, E_{a2} and τ_{02} are parameters for the two Arrhenius processes. These parameters are used for the solid curves in figures 1 and 2.

Sample	E_a (eV)	τ_0 (10^{-12} s)	E_{a1} (eV)	τ_{01} (10^{-12} s)	E_{a2} (eV)	τ_{02} (10^{-8} s)
$TaV_2H_{0.34}$	0.21	13	0.25	3.1	0.082	3.6
$TaV_2H_{0.53}$	0.19	26	0.23	4.8	0.091	1.9
$TaV_2D_{0.17}$	0.25	3.4				

differ from those obtained by NMR spin–lattice relaxation rate measurements. Due to the higher measurement frequencies, the maxima in the spin–lattice relaxation rates occurred at temperatures above 300 K. For those temperatures, τ_2^{-1} is negligible compared to τ_1^{-1} so that only the latter rate would be observed in the NMR experiments.

We interpret the results in the same way [3] as was done for another C-15 Laves-phase system, $ZrCr_2H_x$. Similar to $ZrCr_2H_x$, the attempt frequency for TaV_2H_x, $\tau_1^{-1} \approx 2.5 \times 10^{11}$ s^{-1}, is considerably lower than the hydrogen vibration frequency $\nu_H \approx 4 \times 10^{13}$ s^{-1} typical for Laves-phase hydrides [26]. Thus, classical barrier hopping would not seem to describe the results. Instead, we attribute process '1' to tunnelling between excited states in different interstices, while process '2' is attributed to tunnelling between the ground states [27, 28]. It is interesting to note that our results for $TaV_2D_{0.17}$ do not indicate a contribution from a second process. Due to the strong mass dependence of tunnelling, it is not at all surprising that the relative contributions of tunnelling from excited states as compared to ground states might be different for the two isotopes.

As was discussed above, both NMR and neutron measurements indicate a fast localized motion with the characteristic frequency τ_L^{-1} which persists to low temperatures. This motion gives a double-peaked temperature dependence for the spin–lattice relaxation data. These measurements also indicate that only a fraction of the H (D) atoms participate in the local motion, and this fraction is temperature dependent. The fraction is larger for D than for H [10]. In addition, the hopping rate for D appears to be lower than for H [8]. We think that the most likely explanation for the extra low-temperature attenuation in $TaV_2D_{0.17}$ is due to this localized motion. It appears likely that the hopping rate of H remains well above the ultrasonic measurement frequencies for the temperature range of the measurements, and that is the reason the effect is not seen in TaV_2H_x. Unfortunately, the data obtained for $TaV_2D_{0.17}$ do not permit us to fit the results to a relaxation attenuation model and thus obtain the relaxation parameters for the low-temperature component of the attenuation. Clearly, measurements at lower temperatures are needed. We could not go below 15 K with the present measurements, but we plan to extend the measurements to lower temperatures in the future. Because we only see an attenuation which increases toward lower temperatures and do not see an attenuation peak, it might be argued that the effect is not due to D motion, but is due to something else, e.g. electronic effects. However, it is difficult to understand why such electronic attenuation would be observed in the deuteride, but not in the hydride or the hydrogen (deuterium) free material.

It should be noted that the concentration n in (1) is not necessarily the total concentration of hydrogen in the material. It is not certain that all of the hydrogen contributes to the ultrasonic attenuation. Comparison of the results at $x = 0.34$ and 0.53 indicates that the dependence on n is less than linear, but the quality of the data is not high enough to be certain of the sublinear dependence. In general the resonant ultrasound vibrational eigenmodes depend on a combination of elastic constants; however the 0.50 MHz peak in $TaV_2H_{0.34}$ depends only on

the elastic constant C_{44}. On the assumption that the appropriate n at $x = 0.34$ is that for the *total* hydrogen concentration we find $D = 0.15$ eV for coupling to C_{44} in this material. This value is approximately the same as that found for ScH(D)$_x$ and YD$_x$ [13, 14].

4. Conclusions

Resonant ultrasound spectroscopy measurements on TaV$_2$H(D)$_x$ reveal temperature-dependent attenuation peaks. These peaks can be described in terms of a simple jump process which we associate with long-range hydrogen diffusion. The activation energies and attempt frequencies determined from the ultrasonic measurements are in good agreement with those determined previously from NMR spin–lattice relaxation over the temperature range of the NMR measurements, although the ultrasonic results suggest that the jump mechanism is due to a sum of two Arrhenius processes at lower temperatures. These results show that ultrasound may be used to study hydrogen motion in Laves-phase compounds. In contrast to the NMR and neutron measurements, the ultrasonic results give no indication of a second peak associated with localized motion *in the hydride*. The absence of such a peak in the ultrasonic results could be due to several factors, but the most likely seems to be that the rate of the local H motion remains well above the ultrasonic frequencies throughout the temperature range of the measurements. In contrast to the hydride case or that of the hydrogen- (deuterium-) free material, the results on the *deuteride* showed an increasing ultrasonic loss as the temperature decreased below 50 K. This loss may be due to relaxation attenuation associated with the local motion of the deuterium. Such an interpretation is in accord with the idea that the D hopping rate is lower than that for H and that the fraction of D atoms participating in the localized motion is higher than the corresponding fraction of H atoms. This low-temperature attenuation did not exhibit a peak down to the lowest temperature (15 K) of the present measurements. Measurements at lower temperatures are planned.

Acknowledgments

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