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Ultrasonic attenuation and dispersion due to hydrogen motion in the C15 Laves-phase compound TaV_2H_x

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Abstract

Hydrogen in the C15 Laves-phase material TaV_2H_x has been studied by means of resonant ultrasound spectroscopy over the temperature range of 15–345 K for a series of hydrogen concentrations ($x = 0.00$ – 0.53). Ultrasonic loss peaks and frequency shifts (dispersion) associated with the hydrogen motion were observed, yielding parameters for the hydrogen motion. Hydrogen in these materials is known to occupy the tetrahedral g sites which form a series of interlinked hexagons. The ultrasonic results were associated with H hopping between g -site hexagons. The relaxation rates for $x \leq 0.18$ were best described as a sum of two Arrhenius processes. For $x = 0.34$ and 0.53 only a single Arrhenius process was needed to fit the results, although the presence of a second Arrhenius mechanism could not be over-ruled. A single relaxation rate was sufficient to fit the data; a distribution of rates was not required. The magnitudes of the attenuation and dispersion depended linearly on the hydrogen concentration implying that it is the relaxation of isolated H atoms (the Snoek effect) that is responsible for the mechanical damping. The faster local motion of H reported from nuclear magnetic resonance measurements for motion within g -site hexagons was not observed in the present study. This suggests that the H hopping rate for the local motion remains above the ultrasonic frequencies over the temperature range of study, or perhaps that too few H atoms participate in the local motion.

1. Introduction

Metal–hydrogen materials are important for a number of technological reasons, primarily related to energy storage and battery applications. A high diffusion coefficient of hydrogen in the metal is important for most applications. In addition, the diffusion of a light interstitial such as hydrogen poses challenging theoretical problems [1, 2]. While early work focused on elemental metals [3], more recently there has been an increasing interest in intermetallic

compounds [4] due to their ability to absorb considerable quantities of hydrogen. The local environment of hydrogen in intermetallic compounds is often more complex than in elemental metals due to the large number and variety of interstitial sites in these compounds. This can lead to a series of pathways for the hydrogen motion with the result that the microscopic motion responsible for diffusion is more complicated than in simpler materials. An improved understanding of hydrogen diffusion mechanisms in intermetallic compounds is desirable for both practical and fundamental reasons.

One extensive class of intermetallic compounds is the Laves phase. There is a large number (> 1000) of binary Laves-phase materials [5] with the AB_2 stoichiometry, forming with three symmetries; the C15 cubic, the C14 hexagonal and the C36 structure. All three crystal symmetries have a large number of tetrahedral interstitial sites. Many of these compounds are known to absorb considerable amounts of hydrogen and have been studied extensively with a variety of experimental techniques [6–16]. The present discussion will focus on the C15 structure. There are three different types of tetrahedral site (g , e and b), differentiated by the species of the four surrounding atoms. Each g site is surrounded by two A and two B atoms; each e site by one A and three B atoms; and each b site by four B atoms. It is usually the case that hydrogen occupies the g site in C15 materials [17, 18]. The g sites are arranged in networks of hexagons with the g – g distance within hexagons being less than the g – g distance between hexagons. Each g site is associated with one and only one hexagon.

A fascinating picture is emerging of hydrogen motion in the C15 materials. There appears to be a fast localized motion corresponding to hopping within a hexagon of g sites, and a slower motion corresponding to jumps between hexagons [19–24]. Quasielastic neutron scattering results have shown that for TaV_2H_x the frequency separation between the two mechanisms appears to be the greatest [25]. The lower frequency motion is slower, and the higher frequency motion is faster than in other Laves hydrides. TaV_2 absorbs relatively large amounts of hydrogen, forming stable homogeneous solid solutions of TaV_2H_x ($x \leq 1.7$) [26]. It has been shown that for all H concentrations the single-phase C15 host–lattice structure is maintained down to 4 K. Neutron diffraction results have indicated that hydrogen occupies only the g type (Ta_2V_2) interstitial sites [27, 28]. Both nuclear magnetic resonance (NMR) and quasielastic neutron scattering measurements indicate two frequency scales of hydrogen motion in this material [21, 25]. On the frequency scale of the NMR measurements (10^7 – 10^9 Hz) the spin–lattice relaxation rate data for the hydrogen, $(T_1^{-1})_H$, show two overlapping peaks as a function of temperature. The high-temperature peak was fitted to a single Arrhenius expression and associated with longer-range hexagon-to-hexagon hopping. The lower temperature peak exhibited non-Arrhenius behaviour. This faster motion was attributed to a localized hydrogen hopping within hexagons formed by the g -type interstitial sites and was not frozen out on the frequency scale of the NMR experiment down to 30 K. The local motion demonstrated several unusual features including strong isotope and hydrogen concentration effects.

There is much that is not understood about the hydrogen dynamics in these materials. Thus, it seems desirable to apply other experimental techniques to this problem, such as ultrasound. Mechanical spectroscopy can complement NMR and neutron measurements by exploring a different frequency (and hence temperature) regime. The hopping of hydrogen between nearby interstitial sites has been studied in many systems by means of mechanical spectroscopy (i.e. internal friction, ultrasonic attenuation, etc). Anelastic relaxation occurs in cases where nearby interstitial sites are affected differently by an external stress, leading to a redistribution of the hydrogen occupancy of the sites. If the redistribution rate is comparable to the frequency of the applied stress, mechanical-energy dissipation occurs. The requirements on the local site symmetry in order for anelastic relaxation to occur are described by the selection rules for anelasticity [29]. Although mechanical spectroscopy has been used to study

hydrogen trapped near defects in crystals [30, 31], as well as hydrogen in amorphous metals [32, 33] and quasicrystals [34], the present discussion will focus on hydrogen in solid solution in crystalline metals. For the latter situation two cases can be distinguished. In the Snoek effect, the symmetry of the local sites is such that nearby sites respond differently to an applied stress. The tetrahedral (T) sites in elemental bcc metals are such sites. However, while these sites give rise to a Snoek effect for heavier interstitials such as C, the effect is not observed [35] for H. Apparently this is because the strain field associated with H is cubic despite the tetragonal symmetry of the interstitial site. In the Zener effect the site symmetry is such that anelastic relaxation is not expected for an isolated hydrogen; however, hydrogen–hydrogen interactions lower the site symmetry and lead to anelastic relaxation. This is the situation for the octahedral (O) site in elemental fcc metals [36–41] and the T site in elemental hexagonal metals [42–46]. Depending as it does on H–H interactions, the magnitude of the Zener effect [47, 48] depends on the hydrogen concentration as $x^2(1 - x^2)$ if the occupancy of the sites is not far from random. A simple linear dependence on x is expected for the Snoek effect. In contrast to the large body of work on H relaxation in crystalline elemental metals, there has been relatively little work on crystalline intermetallic compounds [49–51]. As mentioned above, hydrogen occupies only the g sites in TaV₂H_x. The symmetry of these g sites is lower than that of the cubic C15 lattice and thus the selection rules permit a non-zero relaxation strength involving jumps of isolated hydrogen atoms between neighbouring g sites.

The present work is an extension of an earlier study [13] of ultrasonic attenuation in TaV₂H_x. There were several objectives for the present study: one, the ultrasonic study was extended to include dispersion, i.e. the effect of hydrogen motion on the sound velocity; two, the hydrogen concentration was extended to lower values which is relevant to both the Snoek effect and the hydrogen dynamics; three, various experimental improvements allowed for more accurate determination of the parameters of the hydrogen motion than was possible previously; four, it seemed desirable to explore further the applicability of mechanical spectroscopy to intermetallic compounds. The present work found that both the attenuation and dispersion due to H motion could be fitted by the same parameters. The magnitudes of the effects were linear in hydrogen concentration, indicating that isolated hydrogen gives rise to anelastic relaxation in C15 structures. For the entire temperature range studied the parameters of the hydrogen motion are associated with hops between hexagons; the local motion of H was not seen.

2. Experimental details

Polycrystalline ingots of TaV₂ were prepared by arc melting appropriate mixtures of the high-purity constituent elements in an argon atmosphere followed by various annealing procedures. The TaV₂ material was then loaded to varying concentrations of H to form TaV₂H_x, as has been described previously [23].

Using the experimental technique of resonant ultrasound spectroscopy (RUS) [52–54] the ultrasonic attenuation and elastic constants in the TaV₂H_x system were measured for a series of H concentrations (0.00, 0.06, 0.10, 0.18, 0.34 and 0.53). Samples were prepared by cutting approximate rectangular parallelepipeds (RPs) from the button ingots using a low-speed diamond saw. These were then hand polished into accurate RPs suitable for the ultrasonic measurements. Sample edge dimensions and masses were 1–2 mm and 20–50 mg, respectively. The RUS technique excites a large number of the lowest frequency vibrational eigenmodes of RP samples. The samples are placed corner to corner between two piezoelectric transducers. One transducer is used to excite the mechanical eigenmode of a sample with the other detecting the response. From measurements of the resonant frequencies, assuming sample dimensions, density and crystal structure are known, the full elastic modulus tensor can be derived. The

ultrasonic attenuation is found by measuring the quality factor Q of the resonant line shapes. The ultrasonic loss is then given simply as $1/Q$.

Measurements of resonant frequency and attenuation were made over a temperature range of 15–345 K. Above 120 K compressional-mode PZT transducers were used, while at lower temperatures compressional-mode lithium niobate transducers were used. All measurements below room temperature were made in a static low-vacuum atmosphere of He gas (≈ 3 mm of Hg). It was found that this greatly reduced feedthrough of sound across the gap between the transducers. This effect can significantly distort the resonant line shapes, making accurate determination of Q difficult. Measurements were made using a commercial cryostat and temperature controller, with temperature resolution of ± 0.1 K. Measurements above room temperature were made at atmospheric pressure using a commercial oven and temperature controller.

3. Results and discussion

Figure 1 shows ultrasonic loss results for a single mode of TaV_2H_x for each H concentration studied from 15 to 345 K. Each mode presented in figure 1 was within the frequency range of 0.8–1.2 MHz. For all $x > 0$ a clear attenuation peak was observed centred at approximately 220–250 K. Significantly, the attenuation in the hydrogen free material exhibits an almost temperature-independent background with no prominent loss peak. It is immediately clear that the magnitude of the effect increases with increasing H concentration.

The observed attenuation peaks are interpreted as a Debye-type relaxation involving H hopping between adjacent interstitial sites. The ultrasonic loss $1/Q$ due to relaxation is given by [55–57]

$$\frac{1}{Q} = \frac{\Delta c}{c} \frac{\omega \tau_R}{1 + \omega^2 \tau_R^2} \quad (1)$$

where $(\Delta c/c)$ is often referred to as the relaxation strength, $\omega/2\pi$ is the ultrasonic frequency and τ_R is the relaxation time. The quantity Δc is the difference between the unrelaxed (c_U) and relaxed (c_R) elastic moduli; $\Delta c = c_U - c_R$. An explicit expression for the relaxation strength can be calculated for simple systems. An interstitial atom such as hydrogen, which may occupy either of two nearby interstitial sites, can be described as a two-level system. The energy splitting ΔE is given by

$$\Delta E = 2(E_T^2 + A^2)^{1/2} \quad (2)$$

where $2E_T$ is the tunnel splitting and $2A$ is the difference in site energy (asymmetry). For this case it can be shown that the relaxation strength is of the following form,

$$\frac{\Delta c}{c} = \frac{nD^2}{k_B T c} \text{sech}^2 \left[\frac{\Delta E}{k_B T} \right] \quad (3)$$

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 and c is an elastic constant. The formalism may be used even when the tunnelling matrix element E_T is negligible. It is seen that, for D to be non-zero, the two nearby interstitial sites must respond differently to strain, in other words they are inequivalent. Except at very low temperatures it is usually the case that $k_B T \gg \Delta E$ and the $\text{sech}^2[\Delta E/k_B T]$ term approaches unity. In the present study it was found that the data seemed to be fit satisfactorily with equation (3) using this assumption.

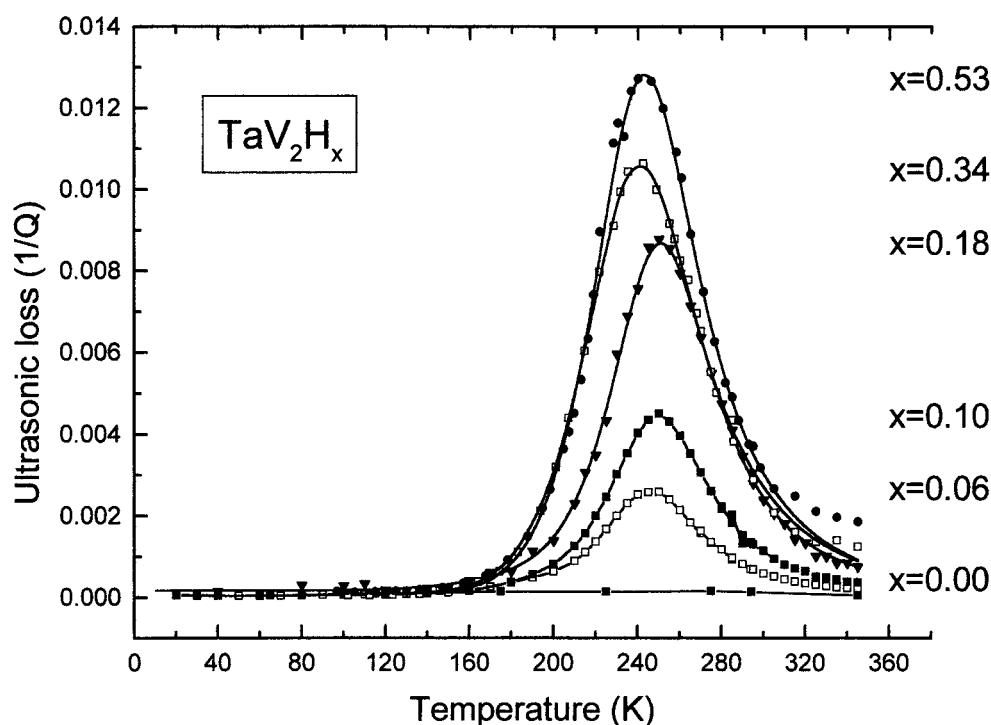


Figure 1. Temperature dependence of the ultrasonic loss in TaV₂H_x. Results are shown for all concentrations studied $x = 0.00, 0.06, 0.10, 0.18, 0.34$ and 0.53 . The full curves represent theoretical fits to the data using the parameters given in tables 1 and 2. All modes are at approximately 1 MHz.

Using the NMR results as a guide, an attempt was first made to fit the data to a simple Arrhenius expression for τ_R ,

$$\tau_R = \tau_{R_0} \exp(E_a/k_B T) \quad (4)$$

where τ_{R_0} is an attempt frequency and E_a is an activation energy. It is assumed that the relaxation time τ_R is approximately the mean dwell time of hydrogen at an interstitial site.

Figure 2 shows attenuation data for TaV₂H_{0.34} at frequencies of 0.675, 0.823 and 1.198 MHz over a temperature range of 100–345 K. Figure 3 shows similar data for the TaV₂H_{0.53} compound at frequencies of 0.643, 0.871 and 1.639 MHz. It can be seen that for these two compositions the fits of the experimental data to equations (1), (3) and (4) are excellent. Importantly, the attenuation data for all modes of each H composition are fit to the same values of attempt frequencies and activation energies. These values indicate that the attenuation peaks are due to the same mechanism responsible for the high-temperature peaks in the NMR experiments [21], which were interpreted as hexagon-to-hexagon hopping. The peaks in the NMR experiments were observed at significantly higher temperatures as those experiments were conducted at much higher frequencies (19.3–90 MHz) than the ultrasonic measurements. The parameters derived from the fits are listed in table 1 with the NMR results of Skripov *et al* [21] for comparison. There is excellent agreement between the activation energies derived by both techniques although there is greater deviation in the attempt frequencies.

We attempted to fit the attenuation results for the lower H concentrations ($x = 0.06, 0.10, 0.18$) to the same model. Figure 4(a) shows attenuation results for TaV₂H_{0.06} at frequencies

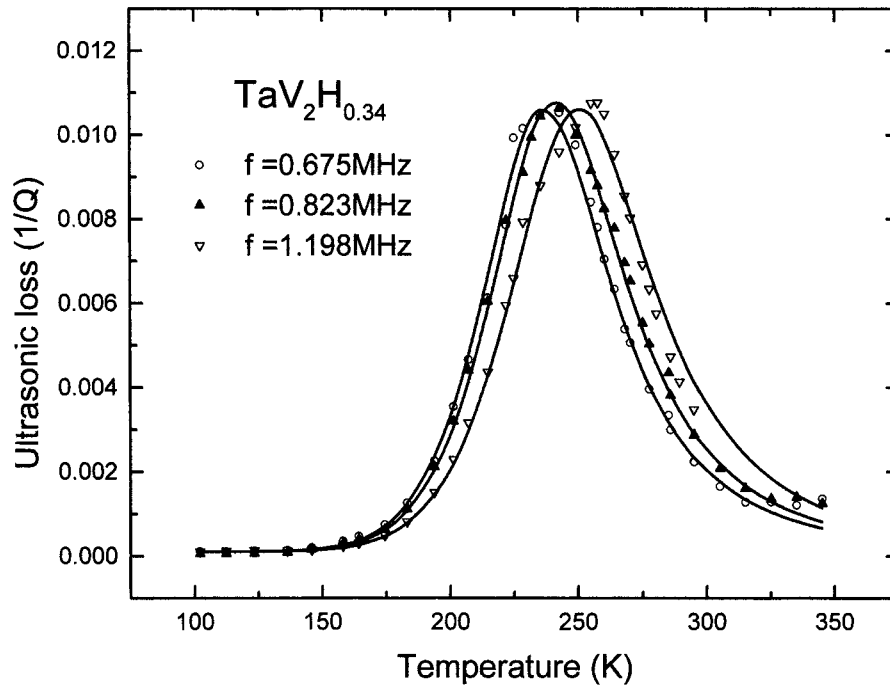


Figure 2. Temperature dependence of the ultrasonic loss in $\text{TaV}_2\text{H}_{0.34}$. The full curves represent theoretical fits to the data using equations (1), (3) and (4) with parameters given in table 1.

Table 1. Parameters of hydrogen diffusion for C15 TaV_2H_x ($x = 0.34$ and 0.53). E_a and τ_{R0} are the parameters derived from fitting to a single Arrhenius process. The fits are shown by the full curves in figures 2 and 3. Estimated uncertainties are ± 0.01 eV in activation energies E_a , and $\pm 30\%$ in pre-exponential factors τ_{R0} . Also included are parameters of hydrogen diffusion for C15 TaV_2H_x ($x = 0.22$ and 0.56) derived from NMR results by Skripov *et al* [21].

Sample	E_a (eV)	τ_{R0} (s)
$\text{TaV}_2\text{H}_{0.34}$ (RUS)	0.22	5.7×10^{-12}
$\text{TaV}_2\text{H}_{0.53}$ (RUS)	0.23	3.9×10^{-12}
$\text{TaV}_2\text{H}_{0.22}$ (NMR)	0.23	2.5×10^{-12}
$\text{TaV}_2\text{H}_{0.56}$ (NMR)	0.24	1.1×10^{-12}

of 0.741, 1.431 and 1.931 MHz over a temperature range of 25–345 K. The full curves in this figure are fits to the data using the form of the relaxation time given by equation (4). A clear ‘undercut’ on the low-temperature side of the attenuation peaks was observed and the shift to higher temperatures for higher frequency modes could not be accounted for as satisfactorily. This small but systematic undercut was also found in fits to all analysed modes of $\text{TaV}_2\text{H}_{0.10}$ and $\text{TaV}_2\text{H}_{0.18}$. Pulsed-field-gradient (PFG)-NMR experiments [58, 59] on a number of Laves-phase materials showed marked deviations from simple Arrhenius behaviour below 200 K for the diffusivity D . The data could be described across the entire temperature range of study (130–430 K) by considering D as a sum of two Arrhenius terms. Motivated by this analysis, we assumed that the relaxation rate in TaV_2H_x is due to the sum of two rates,

$$\tau_R^{-1} = \tau_1^{-1} + \tau_2^{-1} \quad (5)$$

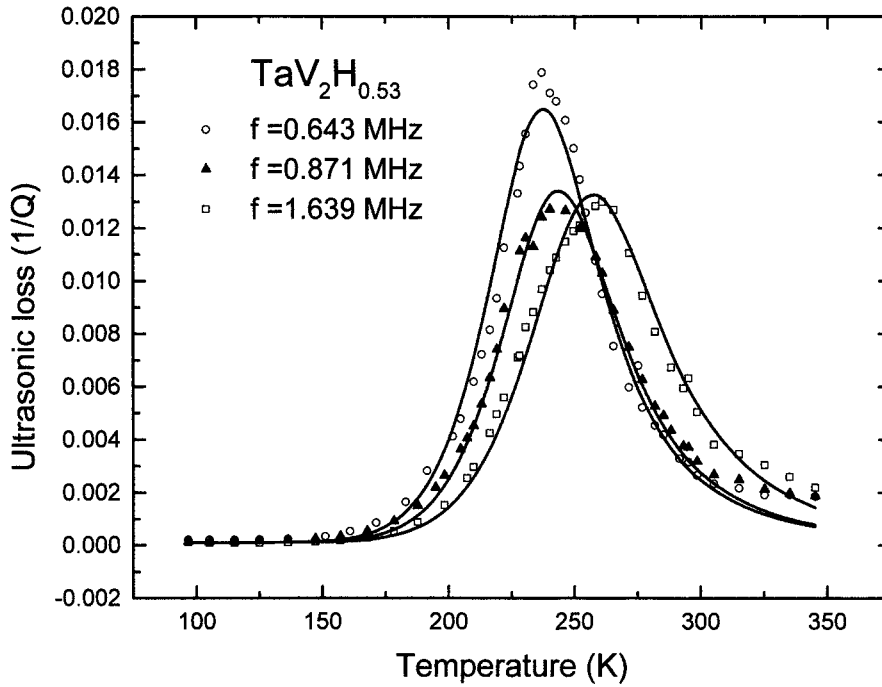


Figure 3. Temperature dependence of the ultrasonic loss in TaV₂H_{0.53}. The full curves represent theoretical fits to the data using equations (1), (3) and (4) with parameters given in table 1.

Table 2. Parameters of hydrogen diffusion for C15 TaV₂H_x ($x = 0.06, 0.10$ and 0.18). The sum of two Arrhenius rates with the parameters E_{a1} , E_{a2} , τ_{01} and τ_{02} was used to describe the ultrasonic attenuation data. The fits are shown by the full curves in figures 4(b), 5(a) and (b). Estimated uncertainties are ± 0.01 eV and ± 0.02 eV in activation energies E_{a1} and E_{a2} , respectively, and $\pm 30\%$ in pre-exponential factors τ_{01} and τ_{02} .

Sample	E_{a1} (eV)	E_{a2} (eV)	τ_{01} (s)	τ_{02} (s)
TaV ₂ H _{0.06}	0.27	0.08	6.2×10^{-13}	5.0×10^{-9}
TaV ₂ H _{0.10}	0.28	0.10	5.2×10^{-13}	11.0×10^{-9}
TaV ₂ H _{0.18}	0.27	0.12	9.6×10^{-13}	6.0×10^{-9}

where

$$\tau_i = \tau_{0i} \exp(E_i/k_B T) \quad (6)$$

with $i = 1, 2$. The experimental data for TaV₂H_x for $x = 0.06, 0.10$ and 0.18 were fit using equations (1), (3), (5) and (6). The experimental data and the results of these fits for $x = 0.06, 0.10$ and 0.18 are shown in figures 4(b), 5(a) and 5(b) respectively. Again three to four modes for each concentration were fit simultaneously to the same parameters and good agreement between the theoretical fits and the experimental data was found. The parameters derived from these fits are presented in table 2.

The theory of relaxation in solids predicts a frequency-dependent shift in the real part of the elastic modulus as well as the attenuation effects. The shift is related to the transition from the relaxed to the unrelaxed elastic moduli as the temperature decreases. The change in the

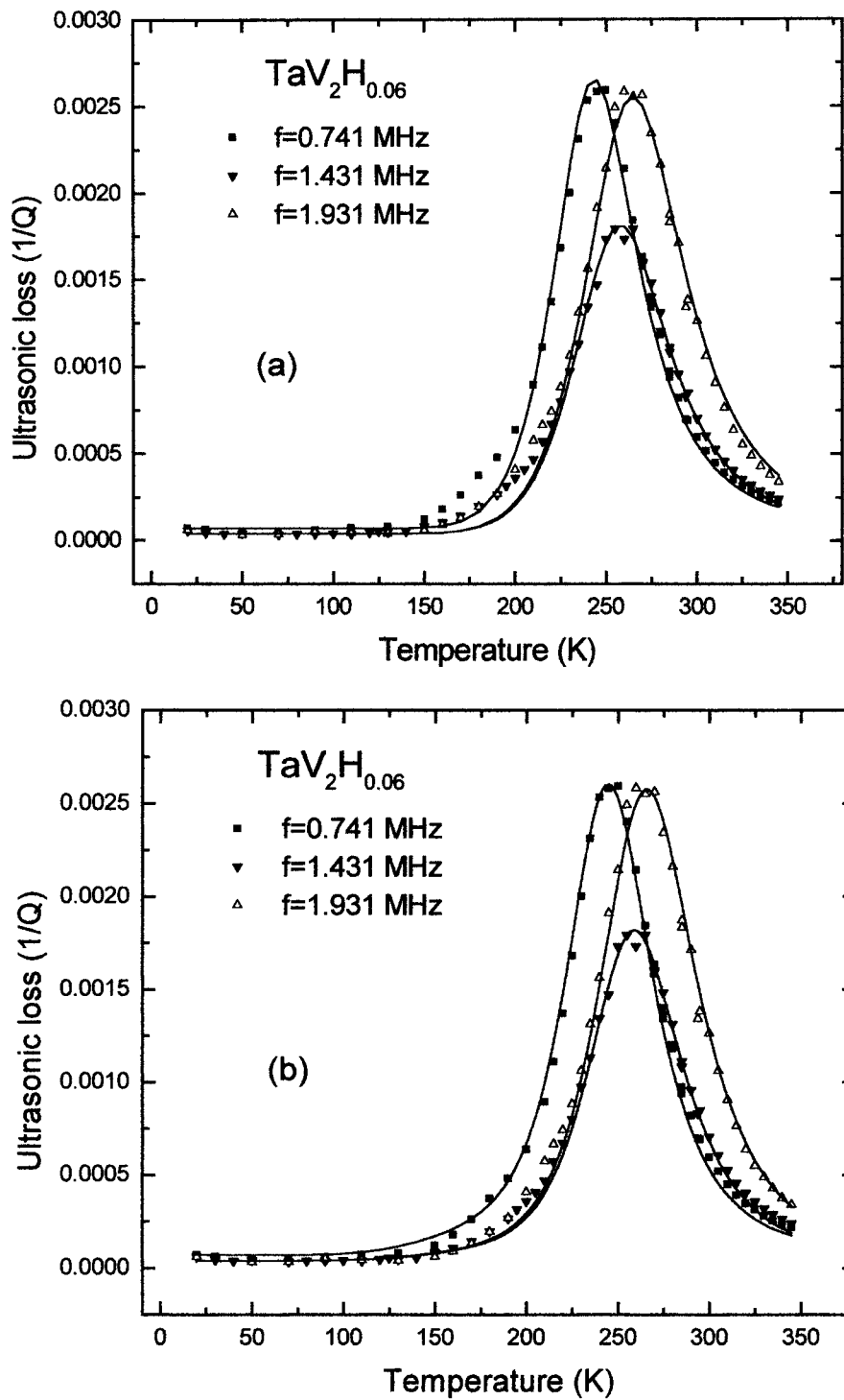


Figure 4. Temperature dependence of the ultrasonic loss in $\text{TaV}_2\text{H}_{0.06}$. (a) The full curves represent theoretical fits to the data using equations (1), (3) and (4). (b) The full curves represent theoretical fits to the data using equations (1), (3), (5) and (6).

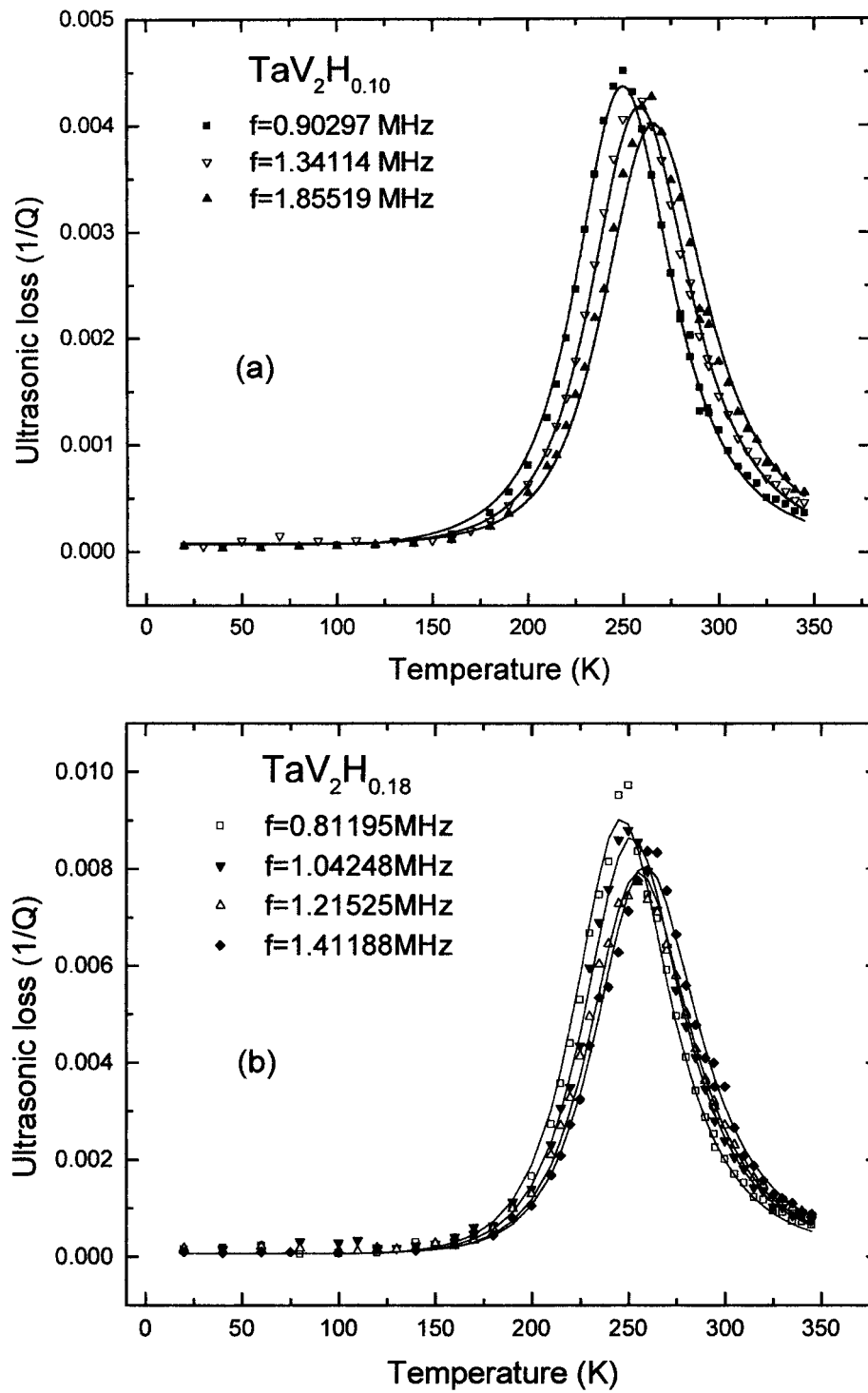


Figure 5. Temperature dependence of the ultrasonic loss in (a) TaV₂H_{0.10} and (b) TaV₂H_{0.18}. The full curves represent theoretical fits to the data using equations (1), (3), (5) and (6) with parameters given in table 2.

elastic moduli δc due to relaxation is given by

$$\delta c = \Delta c \frac{(\omega\tau_R)^2}{1 + \omega^2\tau_R^2}. \quad (7)$$

This change in the elastic moduli then results in a shift δf in the measured mechanical eigenfrequencies

$$\delta f = \left(\frac{\Delta c}{c}\right) \left(\frac{f}{2}\right) \frac{(\omega\tau_R)^2}{1 + \omega^2\tau_R^2} \quad (8)$$

where f was taken to be the room-temperature frequency. Using the relaxation strengths, relaxation times and activation energies derived from the attenuation results (tables 1 and 2) the observed temperature dependence of the resonant frequencies was successfully accounted for by equation (8) for all H concentrations. Figures 6(a) and 6(b) are plots of the frequencies of mechanical eigenmodes versus temperature for TaV₂H_{0.10} and TaV₂H_{0.53}, respectively. Included in these figures are the corresponding attenuation results for that eigenmode on the same temperature scale for direct comparison. Steps in the frequencies are seen. The full curves in figure 6 are theoretical fits to the frequency data using the *same* parameters used to fit the attenuation data. It is seen that the quality of the theoretical fits to both the attenuation and frequency data using the same relaxation parameters is high. In all cases a background term linear in temperature was included in the fits to the frequency data. It can be seen from examination of figures 6(a) and 6(b) that the background temperature dependence of the resonant frequency of TaV₂H_{0.10} is reversed as compared to that of the higher concentration materials. This reversal has been attributed to an electronic band structure effect and is discussed elsewhere [60, 61].

We now turn to a discussion of the parameters of tables 1 and 2. To facilitate the discussion we plot the rates given by these parameters in figure 7. As the figure shows, for the lowest concentration, $x = 0.06$, there is a clear break in the plot at a temperature of about 225 K. The point at which the break occurs decreases in temperature with increasing concentration. The two Arrhenius terms for the lower concentrations being to merge with the single Arrhenius term for the higher concentrations, at least for the temperature range over which there was a measurable attenuation. This suggests that the relaxation rates for the higher concentrations may also be due to a two-Arrhenius process, but these may not be distinguishable from a single-Arrhenius process for the temperature range covered. Figure 7 looks remarkably like the results of Renz *et al* [58] for PFG-NMR diffusion measurements of H in the C15 Laves-phase material ZrCr₂H _{x} . The break occurs at roughly the same temperature and the concentration dependence is very similar. We follow the interpretation of Renz *et al* associating one process with phonon-assisted tunnelling through an excited state and the other with phonon-assisted tunnelling between the ground states. The attempt frequencies for the higher activation energy processes are $\tau_{01}^{-1} \approx 1-2 \times 10^{12} \text{ s}^{-1}$ which are much lower than the typical hydrogen vibration frequencies of $\nu_H \approx 3-4 \times 10^{13} \text{ s}^{-1}$; however these attempt frequencies are closer to the Debye frequency which we estimate [60, 61] as $\nu_D \approx 6 \times 10^{12} \text{ s}^{-1}$ for TaV₂. The theory of quantum diffusion indicates that τ_{01}^{-1} should be of the order of the Debye frequency [1, 62]. Figure 7 indicates that the process 2, attributed to tunnelling between the ground states, becomes weaker as the concentration x increases. The phonon-assisted tunnelling between ground states is expected to be very sensitive to the tunnelling matrix element. It may be that the expansion of the lattice associated with the higher H concentrations leads to an increased tunnelling distance suppressing process 2 at the higher concentrations.

A significant feature of the present results is that a single relaxation rate fits the results (even though this rate may have contributions from two processes), a distribution is not required. This implies that the hexagon-to-hexagon H hopping in TaV₂ involves a specific jump process.

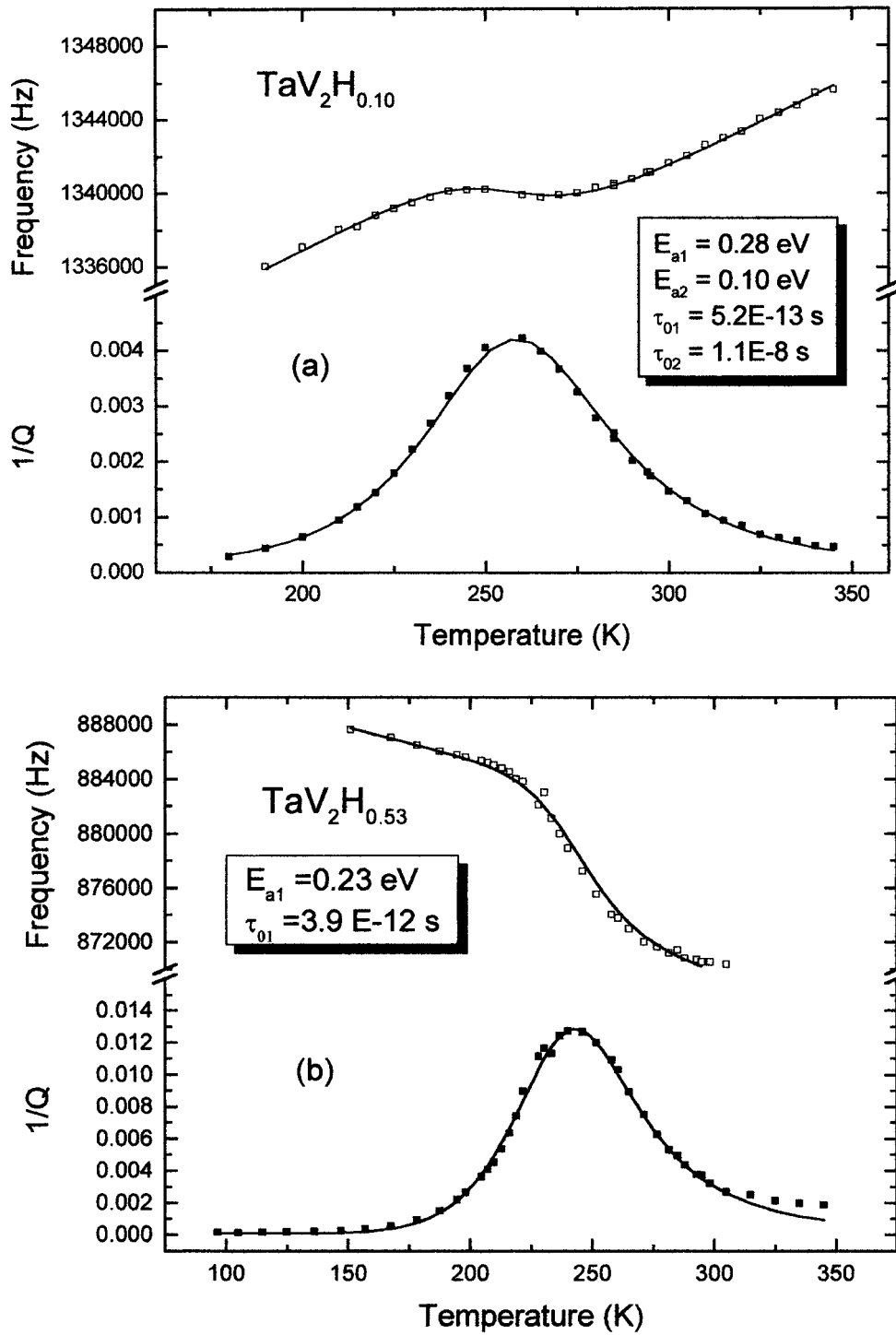


Figure 6. Temperature dependence of the resonant frequency and attenuation of a mechanical eigenmode in (a) TaV₂H_{0.10} and (b) TaV₂H_{0.53}. The full curves represent theoretical fits to the data with parameters given in tables 1 and 2. A background term linear in temperature was included in both frequency fits.

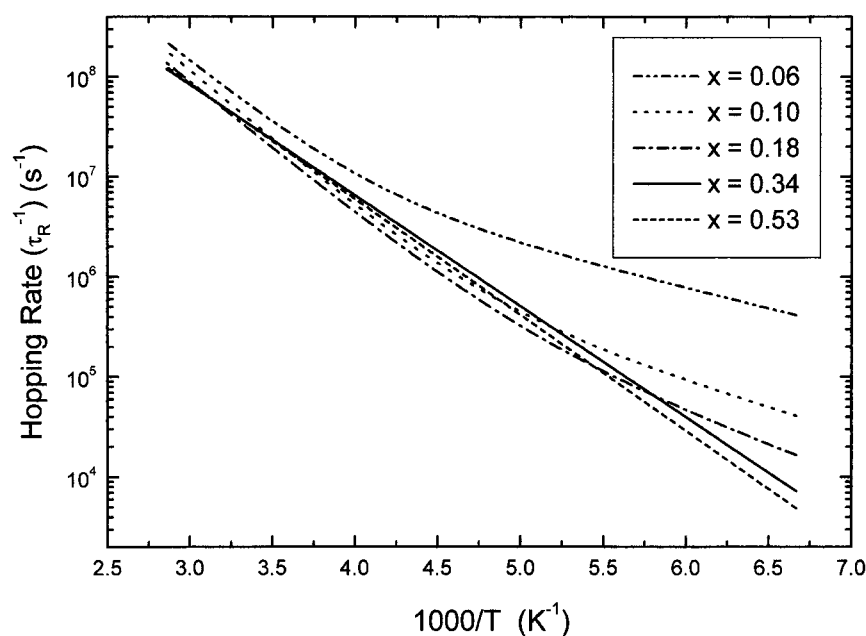


Figure 7. Relaxation rates calculated from the parameters given in tables 1 and 2.

Equation (3) shows that the relaxation strength is given by $nD^2/[k_BcT]$. The temperature dependence is taken into account explicitly in fitting the data. Thus, the fits determine $nD^2/[k_Bc]$. For each concentration, vibrational modes were selected which depended almost entirely (>99%) on the aggregate shear modulus (G). In the present case G depends rather strongly on the hydrogen concentration. Using measured values of G for each concentration [60, 61] we were able to determine the quantity nD^2/k_B . Figure 8 shows this quantity plotted versus n where we assume that n is the hydrogen concentration. The linear dependence shown is exactly what is expected for single interstitial hydrogen atoms, i.e. the Snoek effect. This appears to be an especially clear demonstration of the Snoek effect for hydrogen in crystalline metals. The slope of the plot of figure 8 gives $D = 0.17$ eV. This value is close to that estimated for anelastic relaxation for hydrogen in scandium and yttrium [45, 46].

As has been discussed earlier, both NMR and neutron measurements indicated the presence of a second, more localized H motion in the TaV_2H_x system which persisted down to low temperatures. The neutron results implied that the local motion consists of H hopping about g sites within a hexagon [24, 25]. This motion produced the double-peaked dependence in the proton spin-lattice relaxation results [21]. These measurements indicate that only a fraction of the H atoms participate in the local motion, with this fraction increasing with increasing temperature. The dynamics of this motion are considerably more rapid than that of the longer range hexagon-to-hexagon diffusion. As the local motion is about g sites, it is expected, from symmetry considerations, that this motion should also couple to the ultrasonic strain leading to an attenuation peak. No such peak was found in the present measurements. We believe the most likely reason for this absence is that the hopping rate of the local H motion occurs at frequencies higher than the ultrasonic frequency even down to 15 K. It is also possible that too few H atoms participate in the local motion for the effect to be seen in the present measurements. It is anticipated that attenuation measurements will be made at lower temperatures to look for

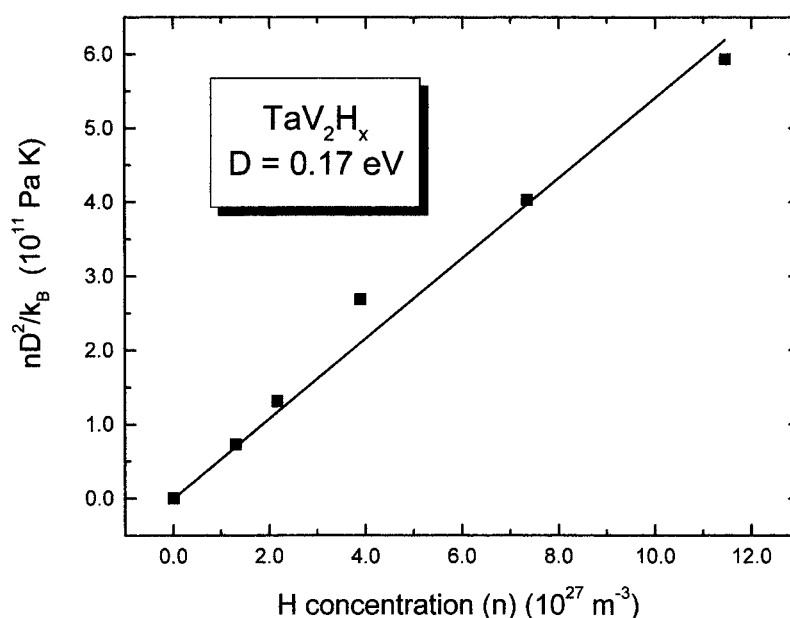


Figure 8. Relaxation strength versus the volume hydrogen concentration (n) for TaV₂H _{x} determined from ultrasonic measurements. The slope of the straight line was used to derive the variation of the energy level splitting with respect to the ultrasonic strain, D .

this effect. An earlier ultrasonic experiment did find evidence for a local motion of D in TaV₂D_{0.17} [13].

4. Concluding remarks

Hydrogen motion in the C15 Laves-phase material TaV₂H _{x} has been studied by means of resonant ultrasound spectroscopy over the temperature range of 15–345 K. Hydrogen concentrations of $x = 0.00, 0.06, 0.10, 0.18, 0.34$ and 0.53 were studied. Attenuation peaks and frequency shifts (dispersion) associated with the hydrogen motion were observed in all the hydrogen containing materials. These effects were centred roughly at 240 K for measurement frequencies of about 1 MHz. For each concentration the two effects, attenuation and dispersion, were fitted by the same parameters (activation energies, attempt frequencies and relaxation strengths) for the hydrogen motion. The parameters of the hydrogen motion indicated that hopping between g -site hexagons was observed, the motion responsible for long-range diffusion. The relaxation rates for $x \leq 0.18$ were best described as a sum of two Arrhenius processes which, following earlier work on other Laves-phase materials, were interpreted as phonon-assisted tunnelling between ground states and between excited states. For $x = 0.34$ and 0.53 only a single Arrhenius process was needed to fit the results, although the two-Arrhenius mechanism cannot be ruled out by the measurements over the given temperature range. The activation energies and hopping rates derived from the ultrasonic data for $x \geq 0.34$ are in good agreement with NMR spin–lattice relaxation measurements [21] probing the same process at higher temperatures. It should be noted that the two-Arrhenius process for the lower concentrations is not necessarily incompatible with the NMR results because that work was performed at much higher frequencies resulting in maxima in T_1^{-1} above 300 K. The

second Arrhenius process, hopping at a rate given by τ_2^{-1} , would have a negligible contribution compared to that of the τ_1^{-1} mechanism at these higher temperatures. It is worth noting that a single relaxation rate was needed to fit the data; a distribution of rates was not required. The magnitudes of the attenuation and dispersion depended linearly on the hydrogen concentration, implying that it is the relaxation of isolated H atoms that is responsible for the mechanical damping. These results show that a Snoek effect due to hydrogen exists in C15 structures.

The faster local motion of H seen earlier by NMR measurements for motion within g-site hexagons, and observed earlier for D by ultrasound, was not observed in the present study. This suggests that the H hopping rate for the local motion remains above the ultrasonic frequencies over the temperature range of study, or perhaps that too few H atoms participate in the local motion at low temperatures to be seen. Future work extending down to 3 K will explore the local motion for both H and D.

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