

**Ultrasonic evidence for hydrogen tunneling in a Laves-phase material:  $\text{TaV}_2\text{H}(\text{D})_x$** 

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Ultrasonic measurements were performed on the *C15* Laves-phase compounds  $\text{TaV}_2\text{H}_{0.18}$ ,  $\text{TaV}_2\text{D}_{0.17}$ , and  $\text{TaV}_2\text{D}_{0.50}$  from low temperatures up to 340 K. The low-temperature end of the measurements was 0.5 K for  $\text{TaV}_2\text{H}_{0.18}$  and 3 K for  $\text{TaV}_2\text{D}_{0.17}$  and  $\text{TaV}_2\text{D}_{0.50}$ . In many *C15* compounds, including  $\text{TaV}_2$ , hydrogen isotopes occupy the interstitial *g* sites, which form a network of linked hexagons. For all three materials, a relatively large attenuation peak was observed near room temperature for measurement frequencies in the range of 1 MHz. This peak was associated with H (D) hopping between hexagons, the rate-limiting step for long-range diffusion. Much smaller attenuation peaks were observed for both H and D in each material at low temperatures and attributed to local motion within a hexagon of *g* sites. These small, low-temperature loss peaks showed totally nonclassical behavior with the H (D) motion exhibiting a very large isotope effect: the relaxation rate for H was over an order of magnitude faster than that for D for similar concentrations. The relaxation rates for the local motion were satisfactorily described by a nonclassical expression with parameters for  $\text{TaV}_2\text{D}_{0.50}$  in agreement with previous NMR measurements for this deuterium concentration. In qualitative agreement with neutron scattering results, it was necessary to assume a temperature-dependent mobile population of H (D) in order to explain the low-temperature attenuation peaks. As further evidence of the nonclassical nature of the motion, the mobile H population was not frozen out on the time scale of the ultrasonic measurements ( $\approx 1$  MHz) down to 1 K. Previously undetected attenuation peaks were observed at an intermediate-temperature range and attributed to an order-disorder transition of the H (D) atoms. It seems likely that this transition is related to the temperature dependence of the mobile population.

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**I. INTRODUCTION**

Recently, much interest has been shown in the study of hydrogen diffusion in Laves-phase materials.<sup>1</sup> Many studies of the cubic (*C15*-type) Laves-phase  $AB_2$  compounds have indicated unusual features for the interstitial motion of hydrogen isotopes. Nuclear magnetic resonance and quasielastic neutron scattering experiments give strong evidence for two frequencies of H (D) motion among interstitial sites in these materials.<sup>2–9</sup> Hydrogen isotopes occupy the *g*-type interstitial sites in the Laves-phase structure. The 96 *g* sites per unit cell (12 per  $AB_2$  formula unit) form a series of linked hexagons. The *g*-*g* distance for neighboring sites within a hexagon is usually shorter than the distance for neighboring sites on different hexagons. The two frequencies of H (D) motion correspond to hopping within a hexagon of *g* sites and between hexagons. This difference between the interhexagon and intrahexagon *g*-*g* distances is related to the ratio of the radii  $R_A/R_B$  of the elements *A* and *B* forming a cubic Laves-phase  $AB_2$  material. For  $\text{TaV}_2$  this ratio is anomalously low, resulting in a large difference between the fast jump rate and the slow jump rate for hydrogen isotopes in this material.<sup>5</sup> The fast motion is of particular fundamental interest because it appears to be dominated by nonclassical effects, including a temperature-dependent H population participating in the motion.<sup>5</sup> The exact form of this temperature

dependence and the origin of the effect are not well known. Recent ultrasonic measurements<sup>10–12</sup> have indicated a strong isotope effect on the fast, localized motion. A low-temperature attenuation peak was observed for D in  $\text{TaV}_2$ , but not for H. Two possibilities were suggested<sup>12</sup> for the lack of a peak for H: the absence of a mobile H population at the low temperatures of the experiment; or, the H motion remained much faster than the approximately 1 MHz frequency of the ultrasound down to helium temperatures. The aim of the present work is to further explore this intriguing low-temperature motion using improved ultrasonic methods. Ultrasonic experiments are ideal for probing the isotope effect because H and D couple to the ultrasound in the same way, in contrast to other probes such as NMR and neutron scattering.

$\text{TaV}_2$  exhibits other interesting behavior that can be investigated by ultrasonic techniques. Previous studies<sup>13,14</sup> on the  $\text{TaV}_2\text{H}(\text{D})_x$  system with  $x(\text{D}) \geq 1.30$  and  $x(\text{H}) \geq 1.15$  have indicated an order-disorder transition below 150 K associated with the long-range ordering of H (D) on the *g* sites. It has been suggested that for lower concentrations, some ordering—perhaps on a local scale—would still exist.<sup>1,15</sup> It is possible that this ordering is connected with the low-temperature, local motion by contributing to the decrease of the mobile population as the temperature is lowered.

The present work is an extension of earlier studies of

ultrasonic attenuation in  $\text{TaV}_2\text{H(D)}_x$ .<sup>10–12</sup> Improvements were made in the equipment that have allowed higher sensitivity in the attenuation measurements. The present paper reports ultrasonic attenuation measurements of  $\text{TaV}_2\text{H}_{0.18}$  over the range of 0.5–100 K and of  $\text{TaV}_2\text{D}_{0.17}$  over the range of 3–100 K. Also reported are results for  $\text{TaV}_2\text{D}_{0.50}$  over the temperature range of 3–340 K. Measurements from 0.5 to 40 K on  $\text{TaV}_2\text{H}_{0.18}$  were made in a 1 T magnetic field. A large attenuation peak near room temperature was observed previously<sup>11</sup> in  $\text{TaV}_2\text{H}_x$  and  $\text{TaV}_2\text{D}_{0.17}$ , and is associated with the slower hexagon to hexagon hopping of H and D atoms. The present article reports a similar peak for  $\text{TaV}_2\text{D}_{0.50}$ . A second, much weaker attenuation peak is observed at low temperature in the deuterated materials and is attributed to the fast, local motion of D. Such a peak was previously seen in  $\text{TaV}_2\text{D}_{0.17}$ , although there was too much scatter in the data to permit a quantitative analysis. An even weaker peak is seen in the current measurements (an order of magnitude smaller than the low-temperature peak in the deuterated materials) at low temperature in the hydrogenated material. The current measurements also indicate a small attenuation peak at intermediate temperatures. This latter peak is consistent with the phenomenology of an ordering transition.

## II. EXPERIMENTAL DETAILS

Polycrystalline ingots of  $\text{TaV}_2$  were prepared by arc melting appropriate mixtures of the high-purity constituent elements in an argon atmosphere followed by various annealing procedures. The  $\text{TaV}_2$  material was then loaded to varying concentrations of H or D to form  $\text{TaV}_2\text{H(D)}_x$  as has been described previously.<sup>16</sup>

Using the experimental technique of resonant ultrasound spectroscopy<sup>17–19</sup> (RUS) the ultrasonic attenuation and resonant frequencies were measured for  $\text{TaV}_2\text{H}_{0.18}$ ,  $\text{TaV}_2\text{D}_{0.17}$  and  $\text{TaV}_2\text{D}_{0.50}$ . With the RUS technique, piezoelectric transducers are used to excite a large number of the lowest-frequency vibrational eigenmodes in samples of well-defined shapes, such as rectangular parallelepipeds. Samples were prepared by cutting approximate parallelepipeds from the button ingots using a low-speed diamond saw. These were then hand polished into accurate rectangular parallelepipeds suitable for the ultrasonic measurements. Sample edge dimensions and masses were 1–1.8 mm and 16–22 mg, respectively. Lithium niobate compressional-mode transducers were used to excite and detect the mechanical resonances. Measurements on  $\text{TaV}_2\text{D}_{0.17}$  from 3 to 100 K, on  $\text{TaV}_2\text{D}_{0.50}$  from 3 to 300 K, and on  $\text{TaV}_2\text{H}_{0.18}$  from 40 to 100 K were made using a commercial cryostat and temperature controller, with the sample in a low vacuum (3 Torr) environment of helium gas. The sample mounting stage was redesigned for this experiment, and care was taken in isolating the entire system from vibrational interference. These steps resulted in lower overall background attenuation and scatter as compared to our earlier work. Measurements on  $\text{TaV}_2\text{H}_{0.18}$  from 0.5 to 40 K were made using a <sup>3</sup>He cryostat at the National High Magnetic Field Laboratory at Los Alamos National Laboratory. Measurements on this sample were also made in

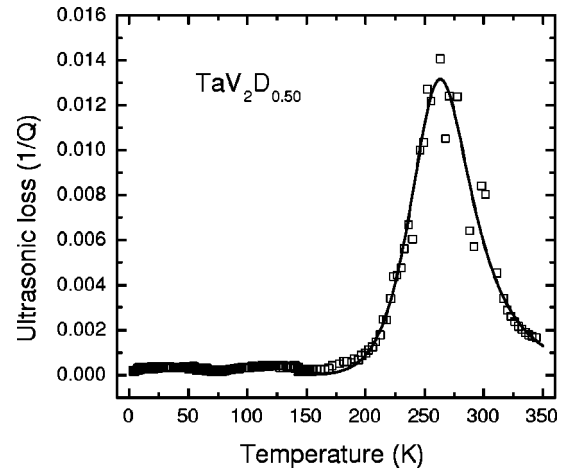


FIG. 1. Ultrasonic loss vs temperature for  $\text{TaV}_2\text{D}_{0.50}$  over the range of 3–340 K. The solid line through the high-temperature peak represents a fit to the data using Eqs. (1), (3), and (4).

a 1 T magnetic field from 0.5 to 40 K. The presence of a magnetic field is known to reduce the background of the ultrasonic attenuation in metals.<sup>20</sup> Measurements above room temperature were made at atmospheric pressure using a commercial oven and temperature controller. The ultrasonic attenuation in the materials is found by fitting the Lorentzian line shapes of the resonant peaks to determine the quality factor  $Q$ . The ultrasonic loss is then given simply by  $1/Q$ .

## III. RESULTS AND DISCUSSION

Figure 1 shows the ultrasonic loss versus temperature over the range of 3–340 K for  $\text{TaV}_2\text{D}_{0.50}$ . As Fig. 1 shows, a relatively large attenuation peak, centered at about 260 K, is observed for the measurement frequency of approximately 1.3 MHz. Similar peaks are observed for  $\text{TaV}_2\text{H}_{0.18}$  and  $\text{TaV}_2\text{D}_{0.17}$  as reported previously.<sup>10,11</sup> These peaks have been attributed to H (D) hopping between hexagons, the relatively slow rate responsible for long-range diffusion. The dependence of this peak on H concentration was reported previously.<sup>11</sup> For D, the amplitude of the peak increases with an increase in concentration, from approximately 0.008 for  $x=0.17$  (Ref. 11) to approximately 0.014 for  $x=0.50$  (Fig. 1). The dependence of the ultrasonic loss on deuterium concentration for this peak will be discussed in more detail below.

Figure 2 shows the ultrasonic loss at low temperatures for  $\text{TaV}_2\text{D}_{0.50}$  on a greatly expanded vertical scale. Two additional peaks, hardly apparent in Fig. 1, are seen in Fig. 2. Similarly, Fig. 3 shows the low-temperature ultrasonic loss in  $\text{TaV}_2\text{D}_{0.17}$  and  $\text{TaV}_2\text{H}_{0.18}$ . Note that the vertical scale for Fig. 3(b) ( $\text{TaV}_2\text{H}_{0.18}$ ) is greatly expanded as compared to Fig. 3(a) ( $\text{TaV}_2\text{D}_{0.17}$ ). In a previous report<sup>12</sup> the low-temperature peaks in  $\text{TaV}_2\text{H}_{0.18}$  could not be observed; the scatter in the data was too great. The data of Fig. 3(b) from 0.5 to 40 K were taken in a 1 T magnetic field, which has the effect of decreasing the overall background attenuation in a metal.<sup>20</sup> This lowered background attenuation permitted the observation of the small peaks in Fig. 3(b). As previously

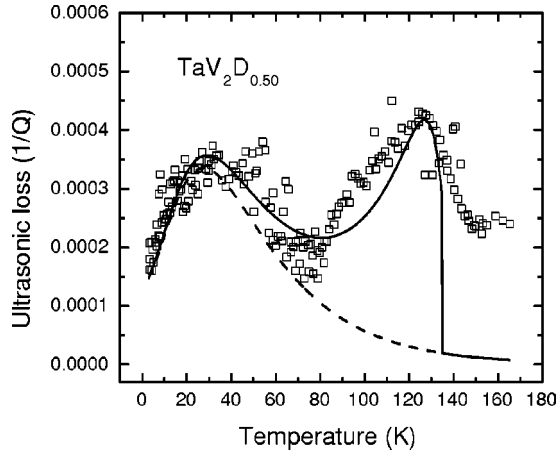


FIG. 2. Expanded view of the low-temperature ultrasonic loss for  $\text{TaV}_2\text{D}_{0.50}$ . The dashed line represents a model of the data using Eqs. (1), (3), (5), and (6) with a distribution of mobilization energies. The solid line shows contributions from all the effects we have modeled.

reported, H-free  $\text{TaV}_2$  exhibited no rise in the ultrasonic attenuation at low temperatures, remaining relatively constant at about  $4 \times 10^{-5}$  up to 100 K, and increasing slightly from this value with increasing temperature.

Figures 1–3, in combination with previous work,<sup>11</sup> indicate several features for the ultrasonic attenuation in  $\text{TaV}_2\text{H(D)}_x$ . (1) There is a relatively large loss peak near room temperature for measurement frequencies near 1 MHz.

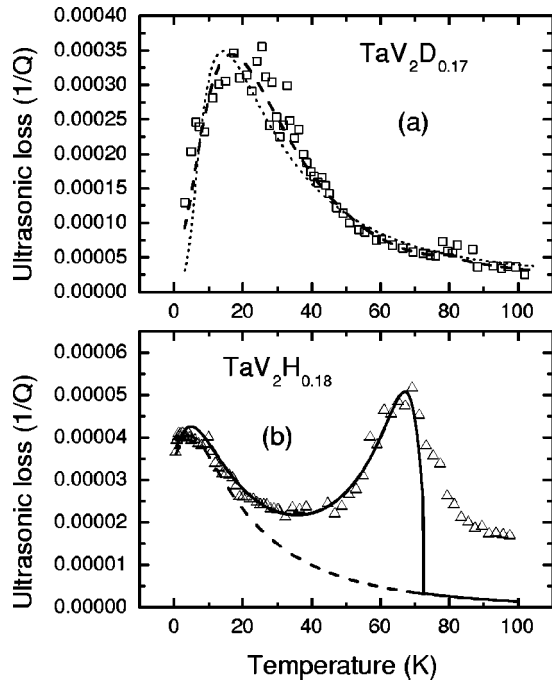


FIG. 3. Low-temperature ultrasonic loss for (a)  $\text{TaV}_2\text{D}_{0.17}$  and (b)  $\text{TaV}_2\text{H}_{0.18}$ . The dotted line in (a) represents a model of the data using Eqs. (1), (3), (5), and (6) with a single mobilization energy. The dashed lines show fits using a Gaussian distribution of mobilization energies. The solid line in (b) shows contributions from all the effects we have modeled.

This peak is well explained as H (D) hopping between hexagons of  $g$  sites. The present article provides additional information about this peak for deuterium. (2) There is a peak at low temperatures. This peak shows a large isotope effect. It appears at about 20 K for deuterium, but at about 1 K for hydrogen. Furthermore, this peak is much weaker for H as compared to D. We will interpret these peaks as H (D) motion within a hexagon of  $g$  sites. (3) There is an intermediate-temperature peak. This peak occurs at about 70 K for  $\text{TaV}_2\text{H}_{0.18}$  and about 125 K for  $\text{TaV}_2\text{D}_{0.50}$ . There is a hint of such a peak at about 80 K for  $\text{TaV}_2\text{D}_{0.17}$ . Based on other work,<sup>13,14</sup> we suggest that these peaks are due to an order-disorder transition of H (D) on the interstitial sites.

We now turn to a more detailed analysis and interpretation of the data. Hydrogen hopping has been studied by use of ultrasonic attenuation in many systems. The motion of a hydrogen isotope between neighboring sites can lead to ultrasonic attenuation. Anelastic relaxation<sup>21</sup> occurs when nearby interstitial sites are affected differently by the applied ultrasonic stress causing the hydrogen to relocate to sites of lower energy. When the applied ultrasonic frequency is comparable to the hydrogen hopping rate, the net effect is dissipation of the input energy. The ultrasonic loss  $1/Q$  due to anelastic relaxation is given by<sup>18</sup>

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

where  $\Delta c/c$  is often referred to as the relaxation strength,  $\omega/2\pi$  is the ultrasonic frequency, and  $\tau_R$  is the relaxation time. The quantity  $\Delta c$  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 a two-level system, which is an appropriate description of an interstitial atom such as hydrogen occupying either of two nearby sites. The energy splitting  $E$  is given by

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

where  $2E_T$  is the tunnel splitting and  $2A$  is the site asymmetry energy. Except at very low temperatures, it can be shown that for this case the relaxation strength is of the following form:<sup>18</sup>

$$\frac{\Delta c}{c} = \frac{n\Gamma^2}{k_B T c}, \quad (3)$$

where  $\Gamma = \partial E / \partial \epsilon$  is the variation of the energy level splitting with respect to the ultrasonic strain,  $c$  is an elastic constant, and  $n$  is the concentration of hydrogen atoms contributing to the attenuation.

For the large attenuation peak at higher temperature a simple Arrhenius expression for the relaxation time,

$$\tau_R = \tau_{R0} \exp\left(\frac{E_a}{k_B T}\right), \quad (4)$$

with activation energy  $E_a$ , can be used along with Eqs. (1) and (3) to fit the data satisfactorily as discussed previously.<sup>11</sup> The solid line in Fig. 1 is a fit to the high-temperature loss peak using Eqs. (1), (3), and (4). This description is valid

over a range of measurement frequencies. Although not shown in the figure, data for two different measurement frequencies were simultaneously fitted for this material. The fit parameters were  $\tau_{R0} = 2.2 \times 10^{-12}$  s and  $E_a = 0.26$  eV. These values are in good agreement with NMR results.<sup>2</sup> The fit also determines  $n\Gamma^2/(k_B c)$ , a quantity related to the relaxation strength as shown in Eq. (3). Using measured values of the aggregate shear modulus for  $c$ , the values for  $n\Gamma^2/k_B$  were calculated. For the  $x = 0.5$  case,  $n = 1.03 \times 10^{28}$  m<sup>-3</sup>, and  $c = 78.4$  GPa (the room temperature value), were used. The quantity  $n\Gamma^2/(k_B c)$  was found to be linearly dependent on the concentration  $n$  for the deuterated samples, as was found for the hydrogenated case.<sup>11</sup> The linear dependence yields a value of the deformation potential  $\Gamma = 0.17$  eV for D in TaV<sub>2</sub>, the same value previously reported for the hydrogenated samples.<sup>11</sup> This linear dependence is an example of the Snoek effect for H (D) in intermetallic compounds.  $\Gamma$  is related to the response of interstitial sites on *different* hexagons to the applied ultrasonic strain. Therefore, it seems reasonable that there is no isotope dependence for  $\Gamma$ . Note that  $1/Q_{\max}$ , which is given by  $n\Gamma^2/2k_B c T_{\max}$ , *does not* depend linearly on the concentration, although  $n\Gamma^2/k_B$  does. This difference is due to the strong concentration dependence of the shear elastic constant.<sup>22</sup>

In contrast to the high-temperature peaks, which are well described as classical Debye peaks with an Arrhenius-type relaxation process, the low-temperature peaks behave quite differently. Skripov *et al.*<sup>2</sup> found that the relaxation time for the low-temperature NMR spin-lattice relaxation data is reasonably well described by the expression

$$\tau_L = \tau_{L0} \exp\left(\frac{-T}{T_0}\right), \quad (5)$$

where  $T_0$  and  $\tau_{L0}$  are fitting parameters. This expression has some justification from quantum diffusion theory, taking into account the effects of barrier fluctuations.<sup>23</sup> We have used this expression to model our low-temperature data. Not only is the relaxation time non-Arrhenius, but the concentration  $n$  of H (D) atoms contributing to the relaxation strength was found to be dependent on temperature. Evidence has been given for a temperature-dependent mobile population.<sup>5</sup> The suggested approach to the description of  $n(T)$  is based on the assumption of some energy gap  $E_0$  between the static and mobile H (D) states. In this case,

$$n(T) = n_0 \frac{\exp(-E_0/k_B T)}{1 + \exp(-E_0/k_B T)}, \quad (6)$$

where  $n_0$  is taken as the total H (D) concentration. Indeed, a temperature-dependent population appears to be required to describe our data. Equations (5) and (6) with mobilization energy  $E_0$  can be used along with Eqs. (1) and (3) to provide a reasonable fit to the low-temperature data for TaV<sub>2</sub>D<sub>0.17</sub>, TaV<sub>2</sub>H<sub>0.18</sub>, and TaV<sub>2</sub>D<sub>0.50</sub>. An application of this model is shown by the dotted line in Fig. 3(a), where a single value of  $E_0 = 1.98$  meV has been used in Eq. (6) to fit the data for TaV<sub>2</sub>D<sub>0.17</sub>. Consistently better agreement between the model and the data was obtained by using a distribution of energies

TABLE I. Parameters of H (D) relaxation for TaV<sub>2</sub>H<sub>0.18</sub>, TaV<sub>2</sub>D<sub>0.17</sub>, and TaV<sub>2</sub>D<sub>0.50</sub>.  $T_0$  and  $\tau_{L0}$  are the parameters derived using Eq. (5). A temperature-dependent mobile population of H (D) atoms was used in place of the total concentration, with a Gaussian distribution of mobilization energies centered on  $E_0$  with width  $\delta E_0$ .

	$\tau_{L0}$ (s)	$T_0$ (K)	$E_0$ (meV)	$\delta E_0$ (meV)
TaV <sub>2</sub> H <sub>0.18</sub>	$2.7 \times 10^{-10}$	50	1.12	1.20
TaV <sub>2</sub> D <sub>0.17</sub>	$8.6 \times 10^{-9}$	30	3.45	1.29
TaV <sub>2</sub> D <sub>0.50</sub>	$5.0 \times 10^{-8}$	38	7.85	3.35

centered on some mean energy value  $E_0$ , i.e., by integrating Eq. (1) from 0 to infinity over a Gaussian distribution of mobilization energies. The dashed line in Fig. 3(a) shows a fit using a Gaussian distribution with a mean value  $E_0 = 3.45$  meV and a Gaussian width  $\delta E_0 = 1.29$  meV. Similarly, the dashed lines in Figs. 2 and 3(b) show fits to the low-temperature peak using the same Gaussian distribution model. The parameters for these fits are given in Table I.

The intermediate-temperature peaks, attributed to an order-disorder transition, give some contribution to the attenuation in the region of the low-temperature peaks. In order to extract the parameters of the low-temperature motion, a simple model for the order-disorder contribution is discussed in what follows. The full lines in Figs. 2 and 3(b) show contributions from both the low-temperature motion just discussed and the order-disorder effect. Before discussing the intermediate-temperature peaks, we make some remarks about the parameters used for the low-temperature peaks. It has been supposed that the existence of the mobilization energy  $E_0$  results from some short-range order among the H (D) atoms. The Gaussian distribution might approximate a spread in the local configurations. For fitting the ultrasonic data, the low-energy side of the Gaussian distribution is much more important than the high-energy side. The reason for this is as follows. Hydrogen isotopes that are in configurations requiring higher mobilization energies will only become mobile at high temperature. At these higher temperatures, the H (D) hopping rate will be so fast, i.e., the relaxation time given by Eq. (5) will be so short that the combined effect of  $\omega\tau_L(T)$  and  $n(T)$  will contribute little to the ultrasonic attenuation. Neutron scattering experiments have been interpreted in terms of an  $n(T)$  that increases linearly at higher temperatures. It is possible that the actual distribution of  $E_0$  is such as to give the observed rise in the ultrasonic attenuation at low temperatures, and the increase in  $n(T)$  at higher temperatures needed to explain the neutron scattering experiments.

It is important to note that the condition  $\omega\tau_L \approx 1$  is never met in the frequency range of our study (approximately 1 MHz). In fact,  $\omega\tau_L \approx 10^{-3}$  at 1 K for TaV<sub>2</sub>H<sub>0.18</sub> and  $\omega\tau_L \approx 0.03$  at 15 K for TaV<sub>2</sub>D<sub>0.17</sub>. In the  $\omega\tau_L \ll 1$  limit, the ultrasonic loss is given by  $1/Q \propto n(T)\omega\tau_L(T)$ . As the temperature decreases  $n(T)$  decreases, but  $\omega\tau_L$  increases. These opposite trends are responsible for producing the peak in the attenuation, not the condition  $\omega\tau_L \approx 1$ . Thus, the present results indicate that the rate of the H motion remains well



above 1 MHz down to 1 K. This model gives only a weak dependence of peak position on measurement frequency, which is in accord with the experimental results. It would be highly desirable to carry out ultrasonic attenuation experiments on this system at 10–100 MHz, which would be an excellent test of the ideas presented here.

Values of  $T_0$  and  $\tau_{L0}$  for  $\text{TaV}_2\text{D}_{0.50}$  have been reported<sup>9</sup> from NMR experiments as 38 K and  $5 \times 10^{-8}$  s, respectively. These values were used to fit our data. The other fitting parameters for the relaxation time in Table I are in accord with the NMR data. The trends in relaxation time as a function of isotope and of concentration are in good agreement with what has been found for other concentrations at higher temperatures;<sup>2,9,24</sup> namely, the H (D) hopping rate is faster for lower concentrations and at least an order of magnitude faster for H than D for a similar concentration.

From the fit of the data to the theoretical expressions, the quantity  $n_0 \Gamma_{\text{low}}^2 / k_B$  is determined, where  $\Gamma_{\text{low}}$  is related to the response of different interstitial sites *within* a hexagon to the applied strain. Assuming that the quantity  $n_0$  is the total concentration of interstitial H (D) atoms, an estimate of  $\Gamma_{\text{low}} = 0.1$  eV is found for the low-temperature motion for all three cases studied (Figs. 2 and 3). It is remarkable that the same value is found for all three cases and indicates a certain self-consistency of the approach. It is reasonable to expect this value to be isotope independent, and to differ somewhat, but not drastically, from the value of  $\Gamma$  found for the response of sites on *different* hexagons (0.17 eV).

We now take a more detailed, yet somewhat qualitative, look at the contribution to the ultrasonic loss for each material from the intermediate-temperature peaks, which we consider to be due to an ordering transition. The intent is not to provide an accurate description of this effect, but to provide an approximate description so as to be able to extract the parameters of the local motion giving rise to the low-temperature peak. If we take the small rise at about 80 K in  $\text{TaV}_2\text{D}_{0.17}$  as an indication of such a peak, then a number of features of these peaks are in accord with heat capacity<sup>15</sup> and neutron scattering<sup>13</sup> studies of the order-disorder transition in  $\text{TaV}_2\text{H(D)}_x$  at higher concentrations. (1) For equal concentrations the transition temperature is higher for D than for H. (2) For a given isotope the transition temperature increases with increasing H (D) concentration. (3) For equal concentrations the magnitude of the effect does not depend strongly on the isotope. (4) For a given isotope the intensities of the superlattice lines indicating the long-range ordering “are found to increase rapidly with increasing  $x$ .”<sup>13</sup> This strong increase is in accord with the fact that the peak at about 125 K in Fig. 2 is much stronger than any possible peak at about 80 K in Fig. 3(a).

For long-range ordering below the transition temperature,  $T_C$ , the relaxation of the order parameter is described by<sup>25,26</sup> the relaxation time  $\tau_C = t_0 / (T_C - T)$ , in the expression

$$\frac{1}{Q} = B \frac{\omega \tau_C}{1 + \omega^2 \tau_C^2}, \quad (7)$$

where  $t_0$  and  $B$  are fitting parameters and  $\omega/2\pi$  is the ultrasonic frequency. This model applies only below the ordering

temperature  $T_C$ . Hence, we make no attempt to account for the contribution of the order-disorder transition to the ultrasonic loss above  $T_C$ . There seems to be no direct evidence for long-range order, such as superlattice lines, at the relatively low H (D) concentrations of our experiments. However, given the strong concentration dependence found for the superlattice lines, it seems that long-range order could exist with a low value of the order parameter at the lower concentrations. Another possibility is that the ordering at the low concentrations is short range. For short-range ordering the expression for the relaxation time would be slightly different from that given above. In any case, we have used Eq. (7) with  $\tau_C \propto (T_C - T)^{-1}$  to obtain a qualitative model of our data, in order to take into account the contribution from this peak to the attenuation in the region of the low-temperature peak. The solid lines in Figs. 2 and 3(b) show the results from adding Eq. (7) to the low-temperature model (indicated by the dashed line), which was discussed previously. The fitting parameters  $t_0$ ,  $T_C$ , and  $B$  for  $\text{TaV}_2\text{D}_{0.50}$  were  $2.4 \times 10^{-6}$  s, 140 K, and  $6 \times 10^{-6}$ , respectively, and for  $\text{TaV}_2\text{H}_{0.18}$ ,  $9.3 \times 10^{-7}$  s, 74 K, and  $1 \times 10^{-6}$ , respectively. The amplitude of the order-disorder peak for  $\text{TaV}_2\text{D}_{0.50}$  is approximately  $4 \times 10^{-4}$ , an order of magnitude larger than the peak for  $\text{TaV}_2\text{H}_{0.18}$ . Assuming the amplitude should be roughly isotope independent, the transition peak in  $\text{TaV}_2\text{H}_{0.18}$  would indicate that an ordering transition in  $\text{TaV}_2\text{D}_{0.17}$  would have an amplitude of approximately  $5 \times 10^{-5}$ . A feature with this amplitude would be virtually lost in the tail of the low-temperature loss peak for this isotope as indicated in Fig. 3(a), but is consistent with the bump in the ultrasonic loss around 80 K in the  $\text{TaV}_2\text{D}_{0.17}$  data.

In general, the interpretation of the ultrasonic data is in accord with the parameters and trends found for the NMR experiments, with one exception. Nuclear spin-lattice relaxation measurements on  $^{51}\text{V}$  in  $\text{TaV}_2\text{H(D)}_x$  have found a stronger relaxation for D as compared to H for the same concentration of the two isotopes.<sup>2</sup> This result has been interpreted<sup>5</sup> as meaning that a larger fraction of the D atoms participate in the local motion as compared to H at the temperatures of the measurements ( $\approx 100$  K). The present ultrasonic measurements at lower temperatures are in disagreement with this interpretation. The ultrasonic results were fit using a mobilization energy for H that is lower than for D. The result is that the population of mobile H is larger than for D in the temperature range of our measurements. In general, neutron scattering, NMR, and ultrasound results all require a temperature-dependent and possibly isotope-dependent population of mobile H (D) atoms to explain the results. These three experimental probes tend to have maximum sensitivity to the H (D) motion in different frequency and temperature ranges. It may be that Eq. (6) just provides a convenient means to describe a temperature-dependent population of H (D) atoms. The actual population may have a more complicated dependence on temperature (and isotope), especially if it is related to the order-disorder transition. The origin of the temperature-dependent population remains unclear.

#### IV. CONCLUSIONS

Ultrasonic techniques were used to study hydrogen motion in  $\text{TaV}_2\text{H}_{0.18}$ ,  $\text{TaV}_2\text{D}_{0.17}$  and  $\text{TaV}_2\text{D}_{0.50}$ , providing further details concerning the peculiar dynamics of hydrogen in Laves-phase materials. The magnitude of the ultrasonic loss for the hexagon to hexagon hopping, the rate-limiting step for long-range diffusion, was found to be linear in D concentration, as was previously found for H. The parameter  $\Gamma$  describing the coupling between  $g$  sites and strain had the value 0.17 eV for both isotopes. The relaxation rate exhibited a small isotope effect and was well described by an Arrhenius-type expression for the H (D) hopping rate.

In marked contrast to these high-temperature peaks, much weaker peaks were observed at lower temperatures that exhibited totally nonclassical behavior. These peaks were attributed to motion within a hexagon of  $g$  sites. The relaxation rate was satisfactorily described by a nonclassical expression, similar to the results from a barrier fluctuation model in the theory of quantum tunneling. The parameters used to describe the relaxation rate for  $\text{TaV}_2\text{D}_{0.50}$  were the same as those used to describe NMR spin-lattice relaxation measurements at higher temperatures on the same material. The relaxation rate for  $\text{TaV}_2\text{D}_{0.17}$  was somewhat faster than that for  $\text{TaV}_2\text{D}_{0.50}$ , in agreement with the concentration dependence found from NMR experiments. Also in qualitative agreement with NMR measurements, the relaxation rate for H was over an order of magnitude faster than that for D for similar con-

centrations. Within experimental error the same value of  $\Gamma_{\text{low}}=0.1$  eV was found for the low-temperature motion for all three materials.

Previously undetected attenuation peaks were observed and attributed to an order-disorder transition of the H (D) atoms among the interstitial sites. These peaks provide experimental evidence for an earlier suggestion that the temperature-dependent mobile population is related to ordering. The main contribution of the present paper is to provide further evidence for the unusual motion of H (D) at low temperatures in the Laves-phase material  $\text{TaV}_2$ , and to show that this motion seems to be dominated by quantum effects. Similar effects probably hold for other Laves-phase  $AB_2$  materials and perhaps rare-earth materials as well. A consistent picture was used to describe the present results. Unanswered questions include the nature of the mobile H (D) population, and the reason for the apparent disagreement between the present ultrasonic measurements and previous NMR measurements as to the fraction of H (D) atoms participating in the local motion.

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