Fast hydrogen motion in the C15 Laves-phase compound $ZrCr_2H(D)_x$ studied by ultrasound

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Abstract
Ultrasonic measurements were made on the C15 Laves-phase material ZrCr$_2$H(D)$_x$ over the temperature range 4–295 K for x(H) = 0.09, 0.15 and 0.31 and x(D) = 0.12. Attenuation peaks associated with H (D) motion between g-site hexagons were observed in all of these materials for measurement frequencies of approximately 1.5 MHz. A strong isotope effect was observed for similar concentrations of H and D and interpreted in terms of quantum mechanisms of diffusion. For temperatures below 200 K, the dominant diffusion mechanism appears to be tunnelling transitions between ground states of hydrogen in adjacent interstitial sites. Comparison with earlier ultrasonic and NMR results suggests that such phonon-assisted tunnelling between ground states is the dominant mechanism of long-range diffusion in many C15 Laves-phase compounds for temperatures below about 200 K. The elastic shear moduli of ZrCr$_2$H$_{0.09}$, ZrCr$_2$H$_{0.15}$ and ZrCr$_2$D$_{0.12}$ were also measured. A small shift was observed in the modulus for each material at a temperature corresponding to the relevant peak in the ultrasonic loss, which is consistent with the interpretation that these peaks are due to H (D) relaxation.

1. Introduction

Due to the small mass of the hydrogen atom, quantum-mechanical effects have been observed for the interstitial motion of H (D) in C15 Laves-phase AB$_2$ materials [1–4]. Hydrogen motion in these materials occurs by hopping among interstitial g sites, which form a series of linked hexagons. Long-range motion is controlled by jumps between hexagons, while a faster, local motion occurs within hexagons. It is expected that the difference between the characteristic rates of the two jump processes originates from the difference between the g–g distances r_1 (within hexagons) and r_2 (between adjacent hexagons). For ZrCr$_2$H(D)$_x$, the ratio r_2/r_1 is 1.07 [1], being closer to 1 than for a number of previously studied Laves phases. Therefore,

the difference between the fast and the slow jump rate for hydrogen motion in this material is expected to be small [5].

Previous studies [6] have shown that the hydrogen in $ZrCr_2$ retains a higher long-range diffusivity at low temperatures than any other metal–hydrogen system with comparable hydrogen concentrations. This work [6] also indicated a change in the effective activation energy for the motion below 200 K. These results were interpreted under the framework of quantum diffusion theory, leading to an understanding of this effect as due to a change in the dominant mechanism from tunnelling between excited states of hydrogen in adjacent g sites to phonon-assisted tunnelling between ground states. The case of extremely fast diffusive motion and the possibility of clarifying the diffusion mechanisms motivate the present ultrasonic investigation.

2. Experimental details

Button ingots of the C15 Laves-phase intermetallic compound $ZrCr_2$ were prepared by arc melting appropriate mixtures of high-purity Zr and Cr in a helium atmosphere followed by annealling in argon at 1300 °C. The preparation of $ZrCr_2H(D)_x$ samples was analogous to that described in [7].

Using the experimental technique of resonant ultrasound spectroscopy [8–10], the ultrasonic attenuation and resonant frequencies were measured for $ZrCr_2H_{0.09}$, $ZrCr_2H_{0.15}$, $ZrCr_2H_{0.31}$ and $ZrCr_2D_{0.12}$ over the range 4–295 K. The 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 were over the range 0.8–2.3 mm. Lithium-niobate compressional-mode transducers were used to excite and detect the mechanical resonances. Measurements over the entire temperature range were made using a commercial ^{4}He cryostat and temperature controller. The ultrasonic attenuation in the materials was found by fitting the Lorentzian lineshapes of the resonant peaks to determine the quality factor, Q. The ultrasonic loss is then given simply by $1/Q$.

The aggregate elastic shear moduli for the hydrogenated and deuterated samples were determined at room temperature by an iterative procedure that minimizes the error between the measured and computed frequencies. In all cases, the frequencies of the lowest 20 resonances were measured with a typical root-mean-square (rms) difference between the measured and computed values of 0.4%. The temperature-dependent values were then calculated from the temperature dependence of a single frequency, 100% dependent on the shear modulus.

3. Results and discussion

Figure 1 shows the ultrasonic loss for $ZrCr_2H_{0.09}$, $ZrCr_2H_{0.15}$, $ZrCr_2H_{0.31}$ and $ZrCr_2D_{0.12}$ over the range 4–295 K. For comparison, the loss is also shown for hydrogen-free $ZrCr_2$. The ultrasonic frequencies are approximately 1.5 MHz. Although there is considerable scatter in the low-temperature data, several meaningful features are apparent. For all hydrogenated samples with $x > 0$ an obvious peak was observed centred at approximately 50–75 K. The attenuation in the hydrogen-free material exhibits an almost constant background with no prominent loss peak. It is clear that the magnitude of the effect increases with increasing H concentration. An obvious peak is also observed in the deuterated material, centred at approximately 160 K, considerably higher in temperature than the peaks for H.

It is instructive to compare the present results with earlier ultrasonic measurements on C15-type $TaV_2H(D)_x$ [2–4, 11]. For each $TaV_2H(D)_x$ sample, two attenuation peaks were

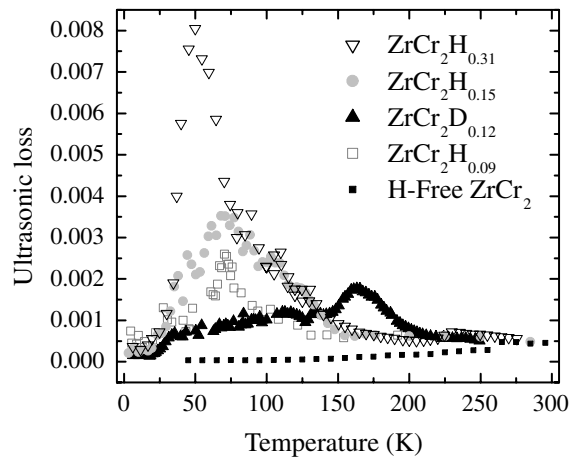**Figure 1.** Ultrasonic loss over the range 4–295 K for ZrCr$_2$H(D)$_x$ with x(H) = 0, 0.09, 0.15 and 0.31 and x(D) = 0.12. The frequencies of the modes range from 1.2 to 1.9 MHz.

observed: a relatively large peak at about 275 K and a much smaller peak at much lower temperatures. The larger peak was associated with H (D) hopping between g-site hexagons, the rate-limiting step for long-range diffusion, while the small peak was associated with motion within a hexagon. The magnitudes of the high-temperature peaks in TaV$_2$H$_x$ were comparable to those of figure 1, which is one reason for associating the latter peaks with hexagon-to-hexagon hopping. Whereas two peaks were observed in TaV$_2$H(D)$_x$ for each sample, a second peak is not obvious in figure 1. The absence of a second peak may be due to the fact that the two hopping rates are expected to be relatively close to each other in ZrCr$_2$H$_x$, so that the small peak due to local motion may overlap the larger peak and be unobservable. In addition, for reasons not entirely clear, the data for ZrCr$_2$H(D)$_x$ are of poorer quality than those for TaV$_2$H(D)$_x$ so that a small peak overlapping the larger peak would be difficult to resolve in figure 1. The high-temperature peaks in TaV$_2$H(D)$_x$ exhibited only a small isotope effect, shifting only a few Kelvin with a change in isotope, while there is a large isotope effect as shown in figure 1. To explain the isotope effect, and other features, we turn to a more detailed analysis.

The hopping of hydrogen has been studied by use of ultrasonic attenuation in many systems. The motion of a hydrogen isotope between neighbouring interstitial sites leads to a relaxation-type ultrasonic loss. Anelastic relaxation [12] occurs when nearby interstitial sites are affected differently by the applied ultrasonic stress, causing the H (D) to relocate to sites of lower energy. When the ultrasonic frequency is comparable to the H (D) hopping rate, the net effect is dissipation of the input energy. The ultrasonic loss, $1/Q$, due to anelastic relaxation is given by [9]

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

where $\Delta c/c$ is often referred to as the relaxation strength, $\omega/2\pi$ the ultrasonic frequency and τ_R the relaxation time. 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
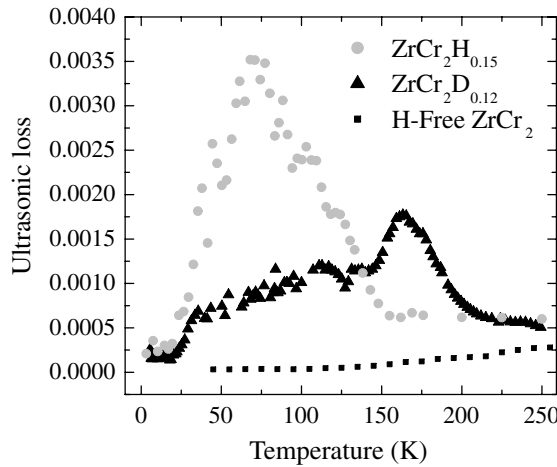
$$E = 2(E_T^2 + A^2)^{1/2}, \tag{2}$$

Figure 2. Details of the ultrasonic loss for $ZrCr_2H_{0.15}$ ($\omega_0/2\pi = 1.2$ MHz) and $ZrCr_2D_{0.12}$ ($\omega_0/2\pi = 1.9$ MHz), showing the strong isotope effect. The loss for $ZrCr_2$ is shown for comparison.

where $2E_T$ is the tunnel splitting and $2A$ is the site asymmetry energy. Except at very low temperatures, it can be shown [9] that for this case the relaxation strength is of the following form:

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

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

Figure 2 shows in more detail the loss peaks in $ZrCr_2H_{0.15}$ and $ZrCr_2D_{0.12}$, indicating a considerable isotope effect. The peak for $ZrCr_2D_{0.12}$ occurs at substantially higher temperatures for approximately the same measurement frequency. This indicates that the D hexagon-to-hexagon jump rate is much lower than that for H. The lower peak height for the deuterated material is approximately accounted for by the slightly lower concentration and the fact that it occurs at a higher temperature, assuming a $1/T$ dependence for the ultrasonic loss. Results [3, 11] for the long-range motion of H (D) in the Laves-phase material, TaV_2, showed peaks that occurred near room temperature. Comparing the temperature at which the peaks occur in $ZrCr_2$ to the room-temperature peaks in TaV_2 indicates that the long-range motion of H (D) in $ZrCr_2$ is, in fact, much faster than in TaV_2. In other words, the hopping rate of hydrogen in $ZrCr_2$ at 70 K is comparable to that in TaV_2 at 275 K.

The results of Renz *et al* [6] for $ZrCr_2$ show that the diffusivity of H fits a two-term Arrhenius expression, one term with parameters corresponding to quantum tunnelling between excited states and one with parameters corresponding to phonon-assisted tunnelling between ground states. The results also suggest that for the temperatures at which our peaks occur, the tunnelling between ground states should be the dominant mechanism of the motion. From diffusivity parameters for $ZrCr_2H_{0.30}$ [6], attempt times $\tau_{R0,i}$ and activation energies $E_{a,i}$ can be calculated for a two-term Arrhenius relaxation time given by

$$\tau_R = \left[\tau_{R0,1}^{-1} \exp\left(\frac{-E_{a,1}}{k_B T} \right) + \tau_{R0,2}^{-1} \exp\left(\frac{-E_{a,2}}{k_B T} \right) \right]^{-1}.$$ (4)
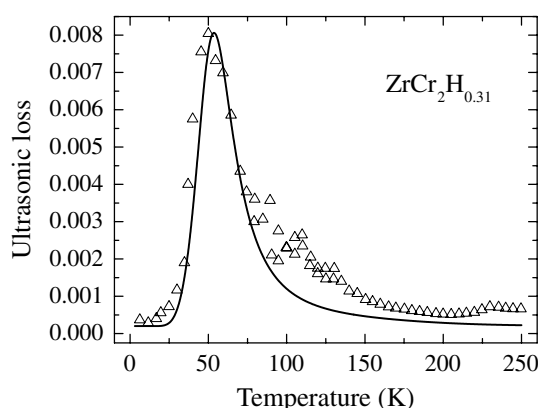
Figure 3. Ultrasonic loss for $ZrCr_2H_{0.31}$. The solid line is a model of the data using equations (1), (3) and (4) with parameters reported in the text.

Parameters for the first term, corresponding to tunnelling between excited states, are $E_{a,1} = 157$ meV as given in [6] and $\tau_{R0,1} = 7.26 \times 10^{-13}$ s. Parameters for the second term, corresponding to tunnelling between ground states, are $E_{a,2} = 39$ meV and $\tau_{R0,2} = 8.43 \times 10^{-10}$ s. Using equations (3) and (4) in equation (1), it can be demonstrated that the excited state term is completely negligible for our measurement temperatures. Using the ground-state term alone, the results are in qualitative agreement with our data, yielding a peak at about 90 K. Better agreement for the case $x = 0.31$ was found by using an activation energy of $E_{a,2} = 23$ meV in the ground-state term. This energy differs somewhat from the value reported in [6]. The solid line in figure 3 shows the results for equation (1), using the parameters, $E_a = 23$ meV and $\tau_{R0} = 8.43 \times 10^{-10}$ s, in a single-term relaxation time. These parameters produce a peak that compares closely with the $ZrCr_2H_{0.31}$ data as shown in figure 3. Because of scatter in the data of figure 3 due to experimental challenges, as well as the presence of some background contributions to the loss, we have not attempted to obtain systematic fits of the peaks to equations (1) and (4). However, the shape and position of the ultrasonic peaks are consistent with results from the pulsed field-gradient NMR experiments. In the temperature range of the peaks of figure 3, the dominant term in the relaxation is the one associated with ground-state tunnelling. Elementary quantum mechanical results for tunnelling of a particle through a barrier, as well as sophisticated theories of quantum diffusion of light interstitials in solids [13, 14] shows that the tunnelling is especially sensitive to the mass of the tunnelling particle. This effect is the more pronounced the higher the barrier through which the particle tunnels. Thus, in $TaV_2H(D)_x$, the long-range motion is believed to involve tunnelling through excited states. Because the associated barrier is low, the isotope effect is small, as observed. In contrast, for $ZrCr_2H(D)_x$ in the temperature range of the present measurement, the motion appears to be tunnelling between ground states. Because the associated barrier is high, the isotope effect is much larger, as shown in figures 1 and 2. The quantity $n\Gamma^2/(k_B c)$, related to the relaxation strength as shown in equation (3), can be estimated using the current results. Using the measured value of the aggregate shear modulus for c, the value for $n\Gamma^2/k_B$ was calculated. For the $x = 0.15$ case, $n = 3.07 \times 10^{27}$ m^{-3}, and $c = 66.7$ GPa (the 100 K value), were used, yielding an estimated value of the deformation potential to be $\Gamma = 0.1$ eV. Previous results [3, 4] for the deformation potential for TaV_2 are similar to this, with $\Gamma = 0.17$ eV for the response of interstitial sites on *different* hexagons to the applied ultrasonic strain, and $\Gamma = 0.1$ eV for the response of different interstitial sites *within* a hexagon to the applied strain.
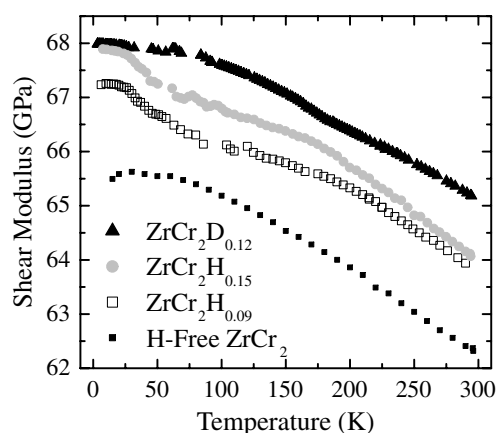
Figure 4. Shear modulus over the range 4–295 K for $ZrCr_2H_{0.09}$, $ZrCr_2H_{0.15}$ and $ZrCr_2D_{0.12}$. The shear modulus for $ZrCr_2$ is shown for comparison.

A two-term Arrhenius relaxation time was found to fit the ultrasonic loss due to H motion in TaV_2 for low H concentrations previously [2, 3]. However, the hexagon-to-hexagon motion, responsible for long-range diffusion, is slower in TaV_2 than in $ZrCr_2$, as discussed above. As a result, the ultrasonic loss peaks occur at around 270 K for ultrasonic frequencies of about 1 MHz. At those temperatures, tunnelling between ground states made only a small contribution. The ultrasonic results on both TaV_2 and $ZrCr_2$, together with the NMR results, indicate that below around 175–200 K, the dominant mode of long-range diffusion in both materials is tunnelling between ground states. This is probably the general case for the C15 materials.

The elastic shear modulus data provide support for the interpretation just discussed. The loss data presented in figures 1–3 are for ultrasonic vibrational modes which depend almost purely on the aggregate shear modulus. Figure 4 shows the modulus, G, for $ZrCr_2H_{0.09}$, $ZrCr_2H_{0.15}$ and $ZrCr_2D_{0.12}$ over the range 4–295 K. For comparison, G is also shown for $ZrCr_2$ from previously reported measurements [15]. The temperature dependence of G for the samples loaded with H (D) is determined by that of a particular resonance frequency, wholly dependent on the shear modulus. A reliable initial fit was not obtained for the highest concentration material. Therefore, G is not reported for $ZrCr_2H_{0.31}$. For typical materials, the temperature dependence of the elastic constants is such that the moduli approach 0 K with zero slope and decrease monotonically with increasing temperature [16, 17]. Figure 4 shows that the moduli of the reported compounds of $ZrCr_2H(D)_x$ behave in a normal fashion over the temperature range of this study. The results also show an increase in the modulus with increasing H content.

Of special interest for the present discussion are the small steps in the shear modulus data seen at about 50 K for the hydrogenated materials. Although difficult to see for the scale of figure 4, an expanded view reveals a clear step in the modulus at about 160 K for the deuterated sample. The theory of relaxation in solids predicts a shift in the real part of the elastic modulus associated with the attenuation effects [9]. The shift is related to the transition from the relaxed to the unrelaxed elastic moduli as the temperature decreases. The change in the moduli, δc, is given by

$$\delta c = \Delta c \frac{\omega^2 \tau_R^2}{1 + \omega^2 \tau_R^2}. \tag{5}$$

The shifts in G occur at temperatures comparable to the temperatures of peaks in the attenuation. The fractional change in the elastic constant, $\Delta c/c$, can be estimated from figure 4. $\Delta c/c$ is related to the maximum value of the ultrasonic loss. The maximum value occurs when the quantity $\omega\tau_R \approx 1$, resulting in the relationship $(1/Q)_{max} = (1/2)\Delta c/c$. Using values taken from figure 4, we estimate for $(1/Q)_{max}$, 0.0035 for ZrCr$_2$H$_{0.09}$, 0.0036 for ZrCr$_2$H$_{0.15}$ and 0.0013 for ZrCr$_2$D$_{0.12}$. These are in remarkably close agreement with values for $(1/Q)_{max}$ taken from figure 2 of 0.0026 for ZrCr$_2$H$_{0.09}$, 0.0035 for ZrCr$_2$H$_{0.15}$ and 0.0017 for ZrCr$_2$D$_{0.12}$. This agreement supports the interpretation of the attenuation peaks as due to H (D) relaxation.

4. Concluding remarks

Ultrasonic measurements on the C15 Laves-phase material ZrCr$_2$H(D)$_x$ over the temperature range 4–295 K revealed attenuation peaks associated with the motion of hydrogen isotopes. For measurement frequencies of approximately 1.5 MHz, the peaks in the hydrogenated material occurred at about 50–70 K, while that for the deuterated material occurred at about 165 K. This strong isotope effect, along with comparison of the present results to earlier pulsed-field gradient NMR results, led to the conclusion that these peaks are due to H (D) hopping between g-type interstitial sites located on different g-site hexagons, the mechanism responsible for long-range diffusion. It was further concluded that this motion involved phonon-assisted tunnelling between the ground states of hydrogen in the interstitial sites. The long-range diffusive motion of H in ZrCr$_2$H$_x$ is much faster than that in a related C15 Laves-phase compound TaV$_2$. Earlier ultrasonic work on TaV$_2$H(D)$_x$ gave attenuation peaks at much higher temperatures, consistent with the slower H (D) motion in this material. Nevertheless, there was an indication of a contribution to the motion at the higher temperatures due to tunnelling between ground states. It seems likely that phonon-assisted tunnelling between ground states is the dominant mechanism for long-range diffusion of H in many C15 Laves-phase materials below about 200 K.

The elastic shear moduli of ZrCr$_2$H$_{0.09}$, ZrCr$_2$H$_{0.15}$ and ZrCr$_2$D$_{0.12}$ were also measured and found to increase with the addition of H or D. The overall temperature dependence was similar to that of typical metals. A small shift was observed in the modulus for each material at a temperature corresponding to the relevant peak in the ultrasonic loss, which is consistent with the interpretation that these peaks were due to H (D) relaxation. This study provides insight into the complicated behaviour of hydrogen motion in Laves-phase intermetallic compounds.

Acknowledgments

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