

Ultrasonic study of hydrogen motion in a Ti-Zr-Ni icosahedral quasicrystal and a 1/1 bcc crystal approximant

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Ultrasonic attenuation measurements have been performed on the Ti-Zr-Ni alloy system over the temperature range 35–335 K. Both a multigrained icosahedral quasicrystal and a 1/1 bcc polycrystalline approximant were studied. The alloys were hydrogenated to a hydrogen to metal ratio of 0.79 for the icosahedral phase and 0.20 for the crystalline phase. Temperature-dependent attenuation peaks were observed in the alloys loaded with hydrogen while the hydrogen-free materials showed no unusual features. For measurement frequencies near 1 MHz the attenuation maxima occurred near a temperature of 250 K for the crystalline phase and 220 K for the icosahedral phase. The results imply that the hydrogen motion is about one order of magnitude faster in the icosahedral phase than in the approximant phase. Whether this result is due to an intrinsic difference between the two Ti-Zr-Ni phases or to a dependence on hydrogen concentration cannot be determined from the present measurements.

I. INTRODUCTION

An understanding of the motion of hydrogen in metals and intermetallics is of considerable importance for both technological and scientific reasons.¹ Metal-hydrogen systems are used in a variety of technological applications, including hydrogen storage materials, metal-hydride batteries, and reversible mirrors. Most applications require a high diffusion coefficient of the hydrogen in the host metal. From the scientific point of view, the interactions of these light interstitials with phonons and conduction electrons result in a rich variety of diffusion mechanisms that are not yet fully understood. The study of hydrogen motion in metals has progressed from simple crystalline systems to more complicated crystalline structures, to amorphous and nanocrystalline metals, and, recently, to quasicrystalline materials. The purpose of this paper is to discuss an ultrasonic investigation into H motion in an intermetallic compound of quasiperiodic order.

Since the discovery of intermetallic² alloys with both long-range aperiodic order and crystallographically forbidden rotational symmetries, a large body of theoretical and experimental work has been devoted to the study of these materials, known as quasicrystals (QC's).³ While the largest class of QC's is the aluminum-based one, the second largest class is based on titanium. Recently a stable Ti-Zr-Ni QC was discovered.^{4,5} Additionally, a closely related 1/1 crystal approximant to the stable Ti-Zr-Ni QC was found.^{6,7} Viano *et al.*⁸ first demonstrated that the Ti-based QC's and their related alloys are able to absorb and desorb considerable quantities of hydrogen making them of potential use for hydrogen storage. The key parameters determining which materials can store hydrogen include the chemical interactions between the metal and hydrogen atoms and the number, type, and size of interstitial sites in the host material. In most transition metal alloys, hydrogen atoms prefer to sit in tetrahedrally coordinated sites. For example, H diffusion in the polytetrahedral Laves phases has been studied extensively with a number of different experimental techniques.^{9–12} The

hydrogen motion in these intermetallic phases tends to be more complex than in simple metals due to the large number and variety of interstices. Icosahedral QC's are also likely dominated by tetrahedral order and thus provide a variety of sites and migration paths for interstitial hydrogen.^{13,14}

There have been few reported studies of hydrogen motion in QC's. Neutron scattering, nuclear magnetic resonance (NMR), and various forms of mechanical spectroscopy including ultrasonic attenuation are the usual methods to study hydrogen hopping in metals. Hydrogen dynamics in icosahedral $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}\text{H}_{150}$ were investigated by neutron scattering.¹⁵ Hydrogen hopping in the $\text{Ti}_{45-x}\text{V}_x\text{Zr}_{38}\text{Ni}_{17}$ system with $x=0.00, 2.00$ was also studied by NMR.^{16,17} These materials were loaded to a hydrogen to metal atom ratio (H/M) as high as 1.88. It appears that there have been no studies of hydrogen motion in QC's and their related alloys by means of any form of mechanical spectroscopy. Ultrasonic measurements provide a powerful complement to NMR and neutron measurements for the study of hydrogen dynamics in materials.^{18,19} The ultrasound couples to the hydrogen differently than the other techniques and is thus a source of additional information. Furthermore, by using ultrasound it is possible to investigate time scales that are difficult or impossible to examine using other techniques. An ultrasonic study of hydrogen motion in QC's can therefore potentially add to the present quantitative and qualitative understanding of hydrogen diffusion in quasiperiodic systems. Based on the dearth of information about hydrogen dynamics in QC's, especially in the frequency range accessible to ultrasound, ultrasonic measurements were made on a Ti-Zr-Ni QC loaded with hydrogen. In addition, measurements were made on a 1/1 bcc crystal approximant to the QC. It appears that there is no information about the hydrogen dynamics in these closely related crystalline systems. A comparison of the ultrasonic attenuation results in the QC and the crystal approximant should give information on the similarity of the hydrogen environments in these two systems.

II. EXPERIMENTAL DETAILS

Alloys of the desired composition $\text{Ti}_{41.5}\text{Zr}_{41.5}\text{Ni}_{17}$ for the *i*-phase QC and $\text{Ti}_{44}\text{Zr}_{40}\text{Ni}_{16}$ for the 1/1 bcc approximant, were prepared by arc melting mixtures of the pure elements on a water-cooled copper hearth in a high-purity Ar gas. The *i*-phase quasicrystal and the *W*-phase approximant were obtained following subsequent annealing procedures described elsewhere.²⁰ Phase purity was confirmed using x-ray and transmission electron microscopy (TEM) investigations. TEM microstructural studies of both samples revealed a distribution of grain sizes the largest diameter being on the order of a few μm .

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 hand polished into rectangular parallelepipeds for the ultrasonic measurements with room-temperature dimensions of $1.321 \times 1.100 \times 1.644 \text{ mm}^3$ and $2.197 \times 1.318 \times 1.621 \text{ mm}^3$ for the *i* and *W*-phase materials, respectively. Measurements of the ultrasonic loss were made using the technique of resonant ultrasound spectroscopy (RUS).^{21–24} The measurements were made using broadband PZT transducers in conjunction with a commercial spectrometer.²⁵ In performing a RUS measurement, a sample is placed corner to corner between two piezoelectric transducers, one of which is used for excitation and one for detection. By sweeping the excitation frequency, a large number of the lowest frequency vibrational eigenmodes of the parallelepiped are excited. The frequencies and the Q values of these modes were measured as a function of temperature. From the frequency measurements it was possible to derive the full elastic constant tensor for both the hydrogen-free *i* and *W* phases; the results of this study are reported elsewhere.²⁰ The ultrasonic loss is generally described as $1/Q$. 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. The Q values of several modes, in a frequency range of 0.5–2.5 MHz, were measured over a temperature range of 35–330 K to determine the loss in the hydrogen-free material. The temperature was controlled using a heater, an electronic controller, and a gas flow cryostat. Thus the sample was in a helium gas atmosphere at approximately ambient pressure during the measurements. A calibrated silicon diode was used for temperature measurements.

The samples were loaded with hydrogen from the gas phase to H/M of 0.79 and 0.20 for the *i* and *W* phases, respectively. Prior to exposure to hydrogen, the samples were first plasma etched in argon and coated with a thin layer of Pd (approximately 15–30 nm). The Pd coating protects the samples from oxidation on subsequent exposure to air and enhances the disassociation of molecular hydrogen. The hydrogenation was carried out in steps at 350 °C. At each step a small amount of hydrogen, corresponding to $\Delta H/M \approx 0.1$, was introduced into the chamber. Additional hydrogen was added only after the pressure reached equilibrium. The total charging time was 13 h for the *W* phase and 44 h for the *i* phase. The H/M ratios were determined directly by the weight gain due to hydrogenation using a Cahn electrobalance with an accuracy of $\pm 5 \mu\text{g}$, and by the hydrogen pressure change upon loading. As expected, the two techniques

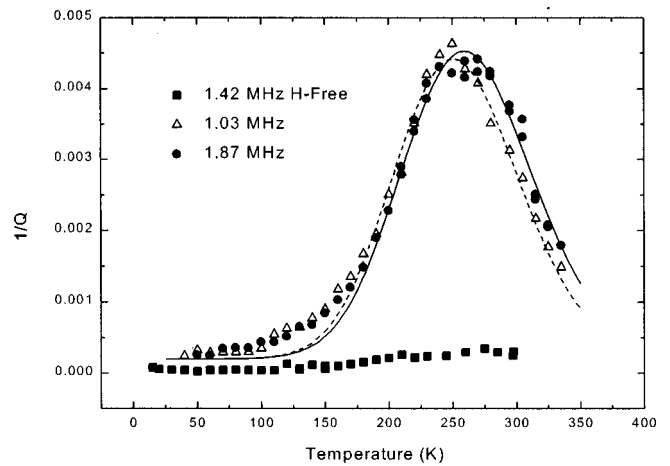


FIG. 1. Ultrasonic loss $1/Q$ vs temperature for *W* phase Ti-Zr-Ni loaded to $H/M=0.20$. The hydrogen-free case is also shown. The symbols represent the data. The solid and dashed lines represent a fit to the data using parameters given in the text. A constant loss of 0.0002 was added to the theoretical curves as a background attenuation.

gave similar estimates of the amount of hydrogen absorbed. Since it is known that the amount of hydride phase formed after the full loading ($H/M=1.6$) is small (less than 5% volume fraction), the samples for the present work (loaded to much lower H/M ratios) were assumed to be single phase. The Q values of several modes were investigated over the same temperature range as for the hydrogen-free material.

III. RESULTS AND DISCUSSION

Figure 1 shows the ultrasonic loss $1/Q$ as a function of temperature for two frequencies in the *W*-phase material. Also shown is the loss in the hydrogen-free material. There is a prominent loss peak in the hydrogenated material with a maximum at about 250 K for a measurement frequency of 1 MHz. The peak shifts to higher temperature with increasing frequency as expected for a thermally activated process. The relatively high loss near the attenuation maximum, combined with the small background signal, presented experimental difficulties. A coherent background signal, due to cross talk between the transmitting and receiving transducers, gave a non-Lorentzian resonance signal in many cases. In cases where the background was not too large compared to the signal from the sample, the data could be reliably corrected for this effect.²⁶ Good results were obtained for five modes in the frequency range of 0.72–1.86 MHz. The solid and dashed lines in Fig. 1 were calculated using parameters from a least-squares fit of the data for these five frequencies. This fit is discussed later in this section. Figure 2 shows attenuation results for the *i*-phase material for both the hydrogen-free and hydrogenated material. There are two apparent differences from the data shown in Fig. 1. First, the attenuation due to hydrogen is higher in the *i*-phase material, likely due to the higher concentration of hydrogen in this material. Second, the attenuation peaks occur at a lower temperature—about 30 K lower—in the *i*-phase material. The solid lines in Fig. 2 are a guide to the eye, not a theoretical fit to the data.

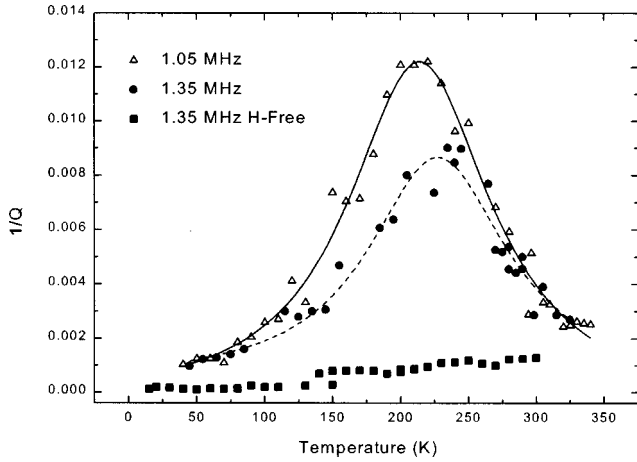


FIG. 2. Ultrasonic loss $1/Q$ vs temperature for i phase Ti-Zr-Ni loaded to $H/M=0.79$. The hydrogen-free case is also shown. The symbols represent the data. The lines are a guide to the eye and *do not* represent a fit to the data.

The higher attenuation in this material leads to greater scatter in the data; it was therefore not feasible to fit the results to theory to obtain an activation energy.

Turning to a more detailed discussion of the data for the W phase, the attenuation peaks are interpreted 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 by²⁷⁻²⁹

$$\frac{1}{Q} = \frac{nD^2}{k_B T C} \frac{\omega \tau}{1 + \omega^2 \tau^2}, \quad (1)$$

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 is the relaxation time. In the classical case tunneling is not a factor and $E_T = 0$. For Eq. (1) it is assumed that $\Delta E \ll k_B T$, which is generally true except at very low temperatures. It is usually assumed that the ultrasonic strain modulation of ΔE is due to a modulation of A , not E_T in which case relaxation attenuation will only occur if the two sites involved are non-equivalent with respect to the applied stress. According to the selection rules for anelasticity,³⁰ anelastic relaxation is only possible if the interstitial site symmetry of the hydrogen is lower than the crystal symmetry. In the present case the location of the hydrogen is unknown so the theoretical rule cannot be applied, but the experimental fact that attenuation peaks are observed indicates that the rule is satisfied in both materials studied. We attempted to fit the data using an Arrhenius expression for τ ,

$$\tau = \tau_0 \exp(E_a/k_B T), \quad (2)$$

where $1/\tau_0$ is an attempt frequency and E_a is an activation energy. An Arrhenius plot of the temperature shift of the peak position with frequency provides an initial value for the

activation energy. It is found that the peaks of Fig. 1 are much broader than can be fit by such a value for E_a . Attempts were therefore made to fit the results with a distribution of activation energies centered about some mean activation energy, i.e., by integrating Eq. (1) over a Gaussian distribution of activation energies. (A distribution of interstitial *site* energies was needed to fit the pressure-composition isotherm data for the W and i phases of Ti-Zr-Ni.³¹) A least-squares fit to the data was made for five frequencies in the range of 0.7–1.9 MHz to determine the parameters E_a , σ , and τ_0 . This procedure gave a reasonably good fit to the data except at the lower temperatures. Below 180 K there is a systematic deviation of the data from the fit for all the measured frequencies. Thus only data above 180 K were used for the least-squares fit. The solid and dashed lines in Fig. 1 show the fit behavior of Eq. (1) for the W phase. A constant background of 0.0002 was added to the theoretical curves to approximately match the measured background attenuation at low temperatures. The fit parameters for the W phase are: $E_a = 0.40 \pm 0.05$ eV, $\sigma = 0.071$ eV, and $\tau_0 = 1.6 \times 10^{-15}$ s. This mean value of 0.40 eV obtained for the activation energy is in good agreement with the value derived from the Arrhenius plot. No other ultrasonic measurements of hydrogen motion in the W phase are available for comparison. However, a comparison may be made to neutron and NMR measurements on the icosahedral phase of Ti-Zr-Ni. In an NMR study of icosahedral $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ loaded to a $H/M = 1.88$ Shastri *et al.*¹⁷ found that a distribution of activation energies was required to fit the ^1H spin-lattice relaxation data with the resulting parameters: $E_a = 0.35$ eV, $\sigma = 0.053$ eV, and $\tau_0 = 1.7 \times 10^{-13}$ s. These parameters for the hydrogenated i phase are similar to those found here from the ultrasonic measurements on the W phase with $H/M = 0.20$. The values for τ_0 , however, differ by a factor of 100, which deserves further comment. The value of τ_0 required to fit the ultrasonic data depends exponentially on the value of E_a chosen. For example, if $E_a = 0.35$ eV were assumed, which is at the bounds of the experimental error, the value of τ_0 required would be 1.5×10^{-14} s, only a factor of 10 different from the NMR results. It is interesting to note that the one neutron-scattering study on i -phase Ti-Zr-Ni revealed an inelastic peak at 130 meV. This corresponds to a hydrogen vibration period of 3.2×10^{-14} s, a value that is quite compatible with our results. (The value of σ required also depends on the value chosen for E_a . With $E_a = 0.35$ eV our optimum value of $\sigma = 0.057$ eV is essentially the same as the NMR value.) A further similarity between the present ultrasonic results on the W phase and the earlier NMR results on the i phase is the deviation between theory and experiment for temperatures below the maximum. This occurs below 300 K for the NMR results (measured at much higher frequencies) and below 180 K in the present case. The fact that such deviations are observed in both experiments suggests that the cause is not specific to the type of experiment and may be an indication of a second relaxation process occurring on a different frequency scale. Alternatively a Gaussian distribution of activation energies may not be appropriate for the major relaxation process; however, the present data do not justify a more complicated approach. The overall evidence indicates that the motion observed with ultrasound in

the *W*-phase material is similar in nature to that observed by NMR in the *i* phase and associated with long-range hydrogen diffusion.

Turning to the ultrasonic results for the *i* phase, Fig. 2 shows considerable scatter in the data associated with the higher attenuation. It was therefore not possible to reliably fit the data to theoretical curves to obtain parameters for the hydrogen motion. Nevertheless, certain conclusions can be drawn from the data. The most important point is that for similar measurement frequencies the peaks occur at lower temperatures in the *i* phase as compared with the *W* phase. From the parameters derived by fitting the *W*-phase attenuation data, the H motion in the *i* phase is estimated to be an order of magnitude faster than that in the *W* phase. Unfortunately, the H/M ratios are different for the two materials, making it difficult to discern whether this faster motion reflects a basic difference between the atomic and structural configuration of the interstitial sites of the two materials, or whether it is due to concentration-dependent effects. Hydrogen diffusion coefficients have been observed to increase as a function of H/M in amorphous materials and attributed to the filling of sites with higher energies at higher H concentrations with a corresponding decrease in the average activation energy.³² Such an effect may be important in the present materials.

IV. CONCLUSIONS

Ultrasonic measurements were made on the Ti-Zr-Ni icosahedral quasicrystal and a closely related 1/1 bcc crystal

approximant. The icosahedral and approximant materials were hydrogenated to a hydrogen to metal ratio of 0.79 and 0.20, respectively. Temperature-dependent attenuation peaks were observed in the alloys containing hydrogen, while the hydrogen-free material showed no unusual features. The peaks shifted to higher temperatures with increasing ultrasonic frequency as expected for thermally activated motion. An activation energy for hydrogen motion of 0.40 ± 0.05 eV was found for the crystal approximant phase. The data did not permit a determination of the activation energy for the icosahedral phase, but the attenuation peaks for this phase clearly occurred at a lower temperature than for the crystalline material. The results indicate that hydrogen motion is about an order of magnitude faster in the icosahedral phase in the temperature range of 225 K. Whether this difference is due to a basic difference in the hydrogen environment in the two materials, or due to a dependence on the hydrogen concentration cannot be determined from the present results. Experiments as a function of hydrogen concentration are planned to answer this question. The results demonstrate that mechanical spectroscopy is a useful tool for studying hydrogen motion in this unusual class of materials.

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