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Ultrasonic relaxation rates in palladium hydride and palladium deuteride

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Ultrasonic attenuation measurements were performed on single-crystal samples of $PdH_{0.67}$ and $PdD_{0.67}$ over the temperature range of 77—300 K. The measured relaxation rates for hydrogen (deuterium) motion exhibit an inverse isotope effect, in agreement with long-range diffusion experiments. While the measured activation energies for hydrogen and deuterium are in good agreement with previous experiments, the attempt frequencies are not. The present attempt frequencies are in good agreement with those expected from the optic-mode frequencies; the previous values were anomalously low.

I. INTRODUCTION

Previous ultrasonic[1,2] and internal-friction[3–9] measurements on palladium hydrides have shown well-defined loss peaks as a function of temperature. These peaks have been attributed to a relaxation involving stress-induced hopping of the hydrogen atoms between octahedral interstitial sites in the host metal lattice. In the case of ultrasonic measurements[2] on single-crystal $PdH_{0.64}$, an Arrhenius plot of the relaxation rate versus inverse temperature gave an activation energy of 0.23 eV, the same as that obtained from other measurements such as NMR (Refs. 10—16) or the Gorsky effect.[17–19] An unusual feature of the ultrasonic measurements was that, although the activation energy was in agreement with that obtained by other methods, the actual relaxation rate determined ultrasonically was an order of magnitude greater than that determined by proton NMR and the Gorsky effect. In other words, the ultrasonically derived attempt frequency was an order of magnitude greater than that derived from other measurements.

Due to the striking differences between the previous ultrasonic results and NMR, we have repeated the earlier ultrasonic measurements on a new single-crystal sample of $PdH_{0.67}$. In addition, we have extended the measurements to palladium deuteride: Measurements are reported for $PdD_{0.67}$. Activation energies and attempt frequencies are reported for both systems. The attempt frequencies are compared with those expected from inelastic neutron scattering measurements of the optic-mode frequencies. Our results are in accord with a recent model proposed by Richards.[20]

II. EXPERIMENTAL DETAILS

The samples used in the present experiments were each cut from a single crystal of palladium obtained from Metal Crystals and Oxides (United Kingdom). The original ingot was approximately 1 cm in diameter and 2.5 cm in length, oriented approximately along the [110] axis. Two specimens were cut from the original ingot, each approximately 0.72 cm long. These two specimens were each prepared with flat and parallel faces which were perpendicular to the [110] direction to within 1°. Charging with H or D was done from the gas phase in a high-pressure cell. The temperature and pressure were varied so as to avoid the mixed α'-α phase region. In order to avoid strains due to concentration gradients, the temperature and pressure were changed slowly, so that the total charging time was about 76 h. Concentration was determined by weight gain. Hydrogen or deuterium was allowed to evolve at room temperature until the concentration in each sample reached 67%, at which point each was stored in liquid nitrogen and only removed for the experiment. Negligible H or D was lost during the experiments.

The standard pulse-echo technique was used to measure the ultrasonic attenuation. Effects due to temperature-dependent properties of the transducer bonding agent were minimized in the usual way by monitoring the heights of two echoes. The longitudinal and two independent transverse waves were propagated along the [110] direction. Data were usually taken by cooling from room temperature to liquid-nitrogen temperature at a cooling rate of 1 K/min or less.

III. RESULTS AND DISCUSSION

Figure 1 shows attenuation results for $PdH_{0.67}$ for the C_L mode (longitudinal waves along [110]), the C mode (transverse waves along [110] polarized along [001]), and the C' mode (transverse waves along [110] polarized along $[1\bar{1}0]$). Within experimental error the peaks for the C_L and C' modes occur at the same temperature while the peak for the C mode occurs about 20 K lower in temperature. (The slightly different frequencies shown in Fig. 1 would only shift the peak about 1 K.) The C-mode peak was also found to occur at a lower temperature in the earlier measurements on $PdH_{0.64}$. This effect will be discussed below.

Measurements on $PdD_{0.67}$ gave results similar to those shown in Fig. 1 with two important differences: (1) a second peak was observed at low temperatures for the longitudinal mode in $PdD_{0.67}$, but not for the transverse modes. This peak will be discussed in a future publication. (2) For a given frequency, the peaks occurred at a lower temperature in $PdD_{0.67}$ than in $PdH_{0.67}$. At 20 MHz the C- and C'-mode peaks occurred at 190 K, while the C-mode peak occurred at 173 K.

Figure 2 shows the attenuation of the longitudinal mode as a function of temperature at several different frequencies for $PdH_{0.67}$. Similar data were collected for $PdD_{0.67}$.

Mazzolai[5] pointed out that internal friction peaks in the Pd-H system could be interpreted in terms of relaxation of vacancy pairs or complexes on the H sublattice in the Pd host metal, a type of Zener relaxation. We have previously shown that ultrasonic attenuation peaks may be interpreted in a similar way.[1] For a single relaxation time τ_R we expect

$$\alpha=\frac{\delta C\omega^2\tau_R}{2vC^R(1+\omega^2\tau_R^2)}\,, \tag{1}$$

where α is the amplitude-attenuation coefficient, $\omega/2\pi$ is the frequency of the ultrasonic wave, v is the wave speed, C^R is the relaxed elastic constant measured at $\omega\tau_R \ll 1$ so that the hydrogen isotopes have time to fully respond, and $\delta C = C^U - C^R$ with C^U being the unrelaxed elastic constant measured at $\omega\tau_R \gg 1$. As shown earlier,[1] the attenuation peaks are too broad to be accounted for in terms of a single relaxation time so that τ_R represents some mean value. We expect τ_R to be given by

$$\tau_R^{-1}=\tau_0^{-1}\exp(-W/kT)\,, \tag{2}$$

where τ_0^{-1} is an attempt frequency and W is an activation energy. τ_R is determined by assuming $\omega\tau_R=1$ at the maxima for curves such as those of Fig. 2. Such an analysis ignores any temperature dependence of $\delta C/C^R$, but we find that such temperature dependence only shifts the results for τ_R by 2—3 K and does not affect in any significant manner the conclusions to be drawn from this work.

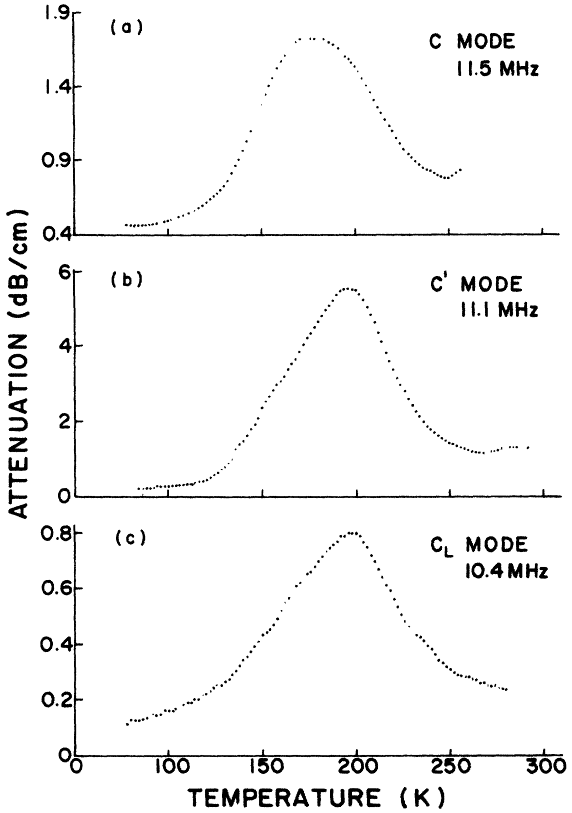

FIG. 1. Attenuation of ultrasonic waves propagating through a single crystal of α'-phase palladium hydride ($PdH_{0.67}$). (a) The C mode propagates along the [110] axis and is polarized along the [001] axis. (b) The C' mode propagates along the [110] axis and is polarized along the $[1\bar{1}0]$ axis. (c) The C_L longitudinal mode propagates along the [110] axis.

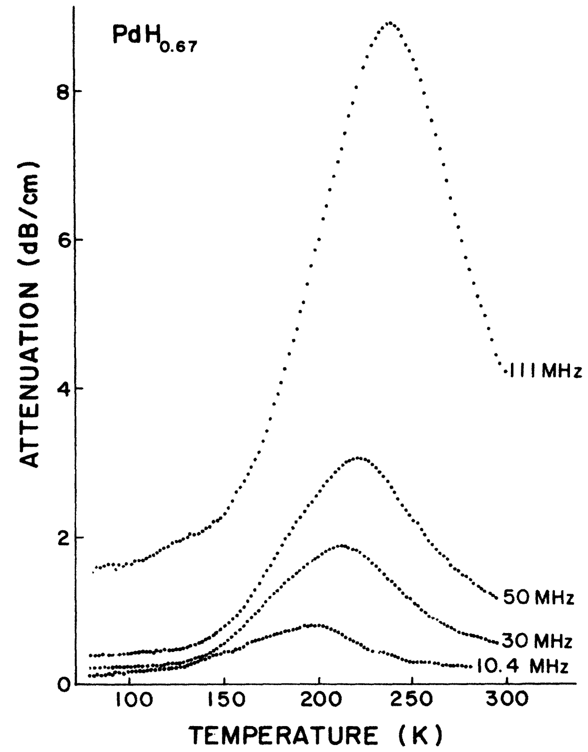

FIG. 2. Attenuation of C_L mode in $PdH_{0.67}$ for various frequencies.

Figure 3 gives an Arrhenius plot of τ_R^{-1} for $PdH_{0.67}$ and $PdD_{0.67}$. The results demonstrate the inverse isotope effect for hydrogen motion which has been known[17,21,22] for some time from macroscopic diffusion measurements. The ratio of the jump rates is in reasonably good agreement with the macroscopic measurements. Extrapolating to 200 K, the data of Völkl *et al.*[17] yield $D_D/D_H=2.2$ for the ratio of the deuterium to hydrogen diffusion coefficients, while the data of Majorowski and Baranowski[23] give 2.0. We find $\tau_{RD}^{-1}/\tau_{RH}^{-1}=2.9$ at 200 K for the ratio of the jump rates. The present results appear to be the first to directly compare the jump rates of the two isotopes in a manner that does not involve the thermodynamic factor.[23]

The straight lines in Fig. 3 are least-squares fits to the data. The activation energies are 0.232±0.008 eV for hydrogen and 0.219±0.008 eV for deuterium. These energies are in good agreement with NMR data (for H) and long-range diffusion data. The prefactors are given in Table I.

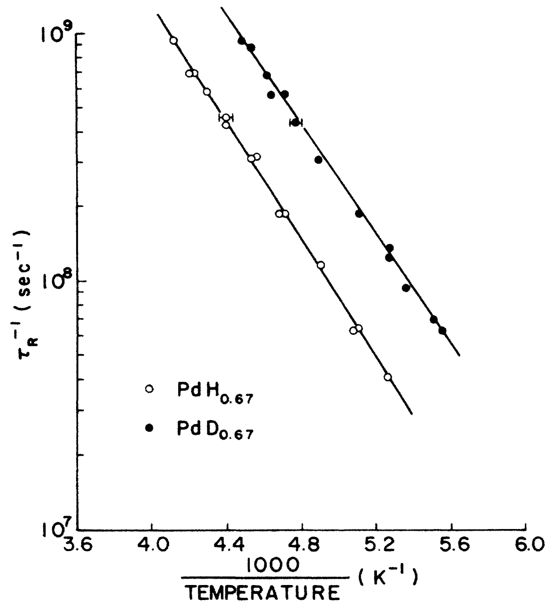

FIG. 3. Inverse relaxation time, τ_R^{-1}, of $PdH_{0.67}$ and $PdD_{0.67}$ determined from present work.

The *C* mode requires special comment. In experiments on two different single crystals of PdH and one single crystal of PdD, the attenuation peak for the *C* mode always occurred at a lower temperature than the other two modes for a given frequency. Unfortunately, a detailed theory for Zener relaxation does not exist for the vacancy concentrations used in the present experiments, although τ_R is usually taken to be approximately equal to the mean time of stay of a vacancy on a particular site. The relaxation for the *C* mode may be somewhat simpler than for the other two modes. The ultrasonic strain imposed by the *C* mode does not change next-nearest-neighbor distances. Thus, as a first approximation, only nearest-neighbor pairs may be considered as contributing to the *C* mode relaxation, whereas both nearest- and next-nearest-neighbor pairs most likely contribute to the relaxation for the other two modes.

Activation energies and attempt frequencies for H motion in palladium hydride have been derived from proton NMR measurements[10-16] for H concentrations ranging from $PdH_{0.56}$ to $PdH_{0.67}$. The NMR determined activation energy is approximately 0.23 eV. A typical value for the attempt frequency is listed in Table I. As can be seen, the NMR value is more than an order of magnitude lower than the ultrasonic values.

Recent experiments[24] on scandium hydride have shown remarkable differences between attempt frequencies derived from proton NMR measurements and scandium NMR measurements. The scandium-derived values were in good agreement with those expected from inelastic neutron scattering measurements of the proton optic-mode frequency, while the proton-derived values were anomalously low. A consideration in understanding these differences seems to be that proton NMR senses labeled particle motion, while the scandium NMR senses vacancy motion.[20]

TABLE I. Prefactors determined ultrasonically (C_L), by NMR, and calculated from the optic vibration frequency for vacancy motion ($8\nu_0^0$). The ultrasonic prefactors are ±50%.

	C_L (sec^{-1})	NMR (sec^{-1})	$8\nu_0^0$ (sec^{-1})
H	6.0×10^{13}	5×10^{12}	1.1×10^{14}
D	8.0×10^{13}		7.7×10^{13}

The ultrasonic relaxation attenuation is only sensitive to site occupancy, which is most easily interpreted in terms of vacancy motion for the present concentrations. A further important point is that, due to the high symmetry of the octahedral site occupied by H (D), no relaxation is expected for an isolated vacancy. Only pairs or complexes contribute. According to the model of Richards, because of strong repulsive interactions at the saddle point, pairs or complexes of vacancies hop much faster than isolated vacancies or labeled particles. Still following the model, the most probable jump for a member of a nearest-neighbor vacancy pair is one which keeps the two vacancies as nearest neighbors. For occupancy of the octahedral sites in the palladium fcc lattice, each vacancy member of a nearest-neighbor pair has four such jumps. The expected attempt frequency[24] is then $4\nu_0^0$, where ν_0^0 is the optic-mode frequency. Since relaxation may occur due to a jump of either member of the pair, the effective attempt frequency is expected to be $8\nu_0^0$. Neutron measurements[25,26] give $h\nu_0^0=58$ meV for PdH and $h\nu_0^0=40$ meV for PdD in the α' phase. Values of $8\nu_0^0$ for H and D are listed in Table I. The agreement with the ultrasonic results is remarkably good.

If we ignore the restrictions on possible jumps imposed by the Richards model, then the expected attempt frequency for a single vacancy is just $Zc\nu_0^0$ where Z is the number of nearest-neighbor octahedral sites and c is the H (D) concentration. Taking $Z=12$, $c\simeq\frac{2}{3}$ for the present case, and multiplying by 2 for a pair of vacancies, we obtain $16\nu_0^0$ for the expected attempt frequency. This value is also in reasonable agreement with the ultrasonic results. Experiments as a function of concentration may distinguish between the two possibilities.

IV. CONCLUSIONS

The relaxation rates derived from ultrasonic attenuation measurements on $PdH_{0.67}$ and $PdD_{0.67}$ are attributed to vacancy jumps on the hydrogen (deuterium) sublattice. The activation energies for the two isotopes are in good agreement with both macroscopic diffusion measurements and proton NMR experiments. In addition, the ratio of the deuterium/hydrogen relaxation rate shows an inverse isotope effect which agrees well with long-range diffusion measurements. Thus, the various experiments apparently sense the same elementary jump process. In marked contrast to the other experiments, the ultrasonically derived attempt frequencies are in good agreement with those expected from neutron scattering measurements of the optic-mode frequencies.

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