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R. Leisure, T. Kanashiro, P. Riedi, D. Hsu

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ULTRASONIC ATTENUATION DUE TO ZENER RELAXATION IN SINGLE-CRYSTAL PALLADIUM HYDRIDE


Department of Physics and Condensed Matter Sciences Laboratory, Colorado State University, Fort Collins, Colorado 80523, U.S.A.

Abstract - Attenuation measurements have been performed for the longitudinal and the two transverse ultrasonic waves propagating along the [110] crystal-line axis in single-crystal α' phase PdH$_{64}$. Attenuation peaks are observed for all three modes. For a measuring frequency of 10.8 MHz the attenuation maxima occur at approximately 190K for the longitudinal and C' transverse modes and approximately 180K for the C$_{44}$ mode. The relative magnitudes of the peaks are interpreted in terms of the gradients of the hydrogen-vacancy ordering energies at nearest and second-nearest neighbor positions.

INTRODUCTION

Hydrogen in palladium hydride occupies the octahedral interstices provided by the fcc palladium lattice and diffuse by jumping between these sites. These octahedral sites themselves form a fcc sublattice. Substoichiometric palladium hydride is analogous to a binary alloy with the constituents of the alloy being hydrogen atoms and vacancies on the hydrogen sublattice. Internal friction peaks in palladium hydride have been shown to be due to a stress-induced ordering of hydrogen and vacancies, similar to Zener relaxation in binary alloys. These internal friction peaks have been found to be asymmetric when the elastic energy dissipation was plotted versus inverse temperature, and this asymmetry has been attributed to a critical temperature for self-ordering in this system. From the shift of the peaks with measuring frequency an activation energy of approximately 0.13 eV has been obtained in the temperature range below 200K.

Hydrogen motion in palladium hydride has also been investigated by nuclear magnetic resonance. These experiments yield values of approximately 0.23 eV for hydrogen motion in the temperature range above 200K. Recently, Gorsky effect measurements on PdH$_{71}$ have determined activation energies which are different at low temperature than at high temperature, with the break occurring at approximately 220K.

We present here ultrasonic measurements on single-crystal PdH$_{64}$. Well-defined attenuation peaks are observed. These peaks are presumably due to the same microscopic stress-induced ordering responsible for the internal friction peaks. As our measuring frequencies are much higher than those used in internal friction, the peaks occur at correspondingly higher temperatures.

EXPERIMENTAL DETAILS AND RESULTS

The palladium single crystal in the form of a cylindrical rod with axis along the [110] crystalline direction was obtained from Materials Research Corporation. The sample on which measurements were made was 1.2 cm long and approximately 1 cm in diameter. Hydrogen was introduced by charging from the gas phase in a pressure cell and furnace. The temperature and pressure were controlled so as to avoid the mixed α-α' phase region. The hydrogen content, 64 atomic percent, was determined by weight gain. The longitudinal and two independent transverse waves were
propagated along the [110] axis. These correspond to the elastic constants 
\( C_L = (1/2)(C_{11} + C_{12} + 2C_{44}) \), \( C' = (1/2)(C_{11} - C_{12}) \), and \( C_{44} \).

Figures 1-3 show the attenuation results obtained at 10.8 MHz. A background 
attenuation, \( \alpha_B \), was subtracted from the measured results; the resulting attenuation 
was then multiplied by \((T-50K)\) and plotted versus inverse temperature. The reason for presenting the data in this form will be discussed below. The attenuation for the \( C_L \) and \( C' \) modes peaked at approximately 190K, while that for \( C_{44} \) peaked at approximately 180K. The magnitude of the attenuation is highly mode-
dependent, being greatest for \( C' \) and least for \( C_L \).

**DISCUSSION**

For a single relaxation process the attenuation is given by

\[
\alpha = (\omega/2\nu)\left(\frac{\delta c}{c}\right) \frac{\omega\tau}{1 + \omega^2 \tau^2} \tag{1}
\]

where \( \alpha \) is the amplitude attenuation coefficient, \( \omega/2\pi \) is the ultrasonic frequency, 
\( \nu \) is the velocity, \( \tau_R \) is the relaxation time, and \( \delta c/c \) is the relaxation strength. It is expected that

\[
\frac{\delta c}{c} \sim (T-T_C)^{-1} \tag{2}
\]

where \( T_C \) is a critical temperature for self-ordering. It is known from neutron 
scattering that palladium hydride undergoes an order-disorder transition in the 
vicinity of 50K, thus we use this value for \( T_C \) in the present analysis. It is also 
expected that

\[
\tau_R^{-1} = \tau_{R0}^{-1} \exp \frac{W}{kT} \tag{3}
\]

where \( \tau_{R0}^{-1} \) is an attempt frequency and \( W \) is an activation energy. We have measured 
the peak position of the longitudinal mode up to 272 MHz and find \( W = 0.23 \pm 0.02 \) 
eV. Our measurements for the other modes are less extensive, but are consistent 
with this value.

Using \( W = 0.23 \) eV and \( T_C = 50K \) we calculated the solid curves shown in Figs. 1-3. 
It can be seen that the experimental curves are too broad to be described by a 
single relaxation time with \( W = 0.23 \) eV. In addition they are asymmetric. In 
order to symmetrize the data, values of \( T_r = 150K \) are needed, which seems unjustifi-
ably high. It seems likely that both the asymmetry and the extra width are due 
to an asymmetric distribution of relaxation times.

With a distribution of relaxation times the maximum attenuation is given by

\[
\alpha_{\text{max}} = \frac{\omega}{2\nu} \left(\frac{\delta c}{c}\right) f_2(0, \beta) \tag{4}
\]

where \( \beta \) is a measure of the distribution width. In the case of a single relaxation 
time as in Eq. (1), \( f_2(0, \beta) = (1/2) \). Nowick and Berry have tabulated the function 
\( f_2(0, \beta) \) for the case of a Gaussian distribution of relaxation times. Although the 
shapes of the curves in Figs. 1-3 are not described by such a distribution, we will 
as a first approximation use the tabulated results of \( f_2(0, \beta) \) for a Gaussian
Fig. 1. Ultrasonic attenuation of 10.8 MHz longitudinal waves propagating along the [110] axis in PdH\textsubscript{0.64}.

Fig. 2. Ultrasonic attenuation of 10.8 MHz transverse waves propagating along the [110] axis and polarized along the [110] axis in PdH\textsubscript{0.64}.
distribution to account for the reduction in $\alpha_{\text{max}}$ caused by a spread of relaxation times. We find $f_2(0, \delta) = 0.33, 0.32,$ and $0.30$ for the $C_L$, $C'$, and $C_{44}$ modes, respectively. Using these values, Eq. (4), and the maxima from Figs. 1-3 we find, $(\delta C_L/C_L) = 3.3 \times 10^{-3}$, $(\delta C'/C') = 1.2 \times 10^{-2}$, and $(\delta C_{44}/C_{44}) = 3.7 \times 10^{-3}$. A more detailed analysis of the curves might change these values somewhat, but would not likely change their relative magnitudes.

The Zener relaxation strength in concentrated alloys has been investigated theoretically by Welch and LeClaire. We apply their results to the present case and take the alloy to be hydrogen atoms and vacancies on the hydrogen sublattice. We take their results for the high temperature limit. This limit corresponds to the short-range order parameters being small. Since the peaks in the present case occur near 190K, while the temperature for self-ordering is near 50K, the high temperature limit approximation should be a good one. They find

\[
\frac{\delta C}{c^R} = \frac{N}{V} \frac{2(1-x)^2}{kT} \sum_{i=1}^{\infty} \sum_{j=1}^{z_i/2} \left( \frac{dv_j^i}{dc} \right)^2
\]

where $N/V$ is the number of interstitial sites per unit volume, $x$ is the hydrogen concentration and $c^R$ is the elastic constant corresponding to the particular strain. The index $i$ refers to the various neighbor shells, nearest neighbor, next-nearest neighbor, etc., relative to some particular lattice site chosen as the origin. $z_i$ is the number of atoms within the $i$-th shell and $j$ refers to the $z_i/2$ positive directions within the shell. $V_j^i$ is the hydrogen vacancy ordering energy for the site $(i,j)$ relative to the origin.

We assume that the hydrogen interactions may be described by central forces. Then $dV_j^i/dc$ may be written as $(dV_j^i/dr_j^i)(dr_j^i/dc)$. Furthermore $dV_j^i/dr_j^i$ is replaced by...
\( \frac{dV_i}{dr_i} \), the gradient of the ordering energy at shell \( i \). The sum over \( j \) in Eq. (5) then reduces to a geometric factor for each neighbor shell which depends on the particular strain mode \( \varepsilon \) being propagated. Using \( N/V = 4/a_0^3 \) for the fcc lattice we find

\[
\frac{\delta C_{44}}{C_{44}} = \frac{4x^2(1-x)^2}{a_0C_{44}k(T-T_0)} \left[ \frac{w_1}{4} + \frac{3w_3}{2} + \ldots \right] 
\]

(6a)

\[
\frac{\delta C'}{C'} = \frac{4x^2(1-x)^2}{a_0C'k(T-T_0)} \left[ \frac{w_1}{8} + \frac{w_2}{2} + \frac{3w_3}{4} + \ldots \right] 
\]

(6b)

where \( w_i \equiv (dV_i/dr_i)^2 \).

In addition we find

\[
\delta C_L = 2\delta C_{44} + \delta C' .
\]

(7)

This last equation apparently results from the central force approximation.

Using the values of \( \delta c/c \) derived earlier, together with the values of the \( c' \)s measured previously, we have determined experimentally, all in units of N/m²:

\[
\delta C_L = 8.6 \times 10^8, \quad \delta C_{44} = 2.3 \times 10^8, \quad \text{and} \quad \delta C' = 3.5 \times 10^8.
\]

Here we have applied a \( T^{-1} \) correction to \( \delta C_{44} \) to take into account the fact that this peak occurred at 180K, rather than 190K. The value above corresponds to the expected value at 190K. Inserting the above values of \( \delta C_{44} \) and \( \delta C' \) into Eq. (7) yields \( \delta C_L = 8.1 \times 10^8 \) N/m², in good agreement with the measured value.

We now interpret our results in terms of the \( w_i \). Since there are only two independent equations for the \( \delta c' \)s we can only hope to obtain values for two of the \( w_i \).

We find \( |dV_1/dr_1| = 5.9 \times 10^{-11} \) N and \( |dV_2/dr_2| = 4.1 \times 10^{-11} \) N. It is clear that forces beyond nearest neighbors are quite important. Of course, what is really measured is the sum of the interaction terms in Eqs. (6), and we cannot be sure that neighbors more distant than second nearest do not also contribute to the results.

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*Permanent address: Department of Physics, Faculty of Engineering, Tokushima University, Tokushima 770, JAPAN.
+Permanent address: Department of Physics, University of St. Andrews, St. Andrews, Fife, SCOTLAND.