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Novel ultrasonic attenuation peak in α'-PdD$_x$

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An unusual ultrasonic attenuation peak has been observed in PdD$_x$. The peak is seen only for longitudinal waves, not transverse waves; and it is observed only in the deuteride, not the hydride. The relaxation strength of the peak increases rapidly with temperature. The data are well described in terms of a simple model involving relaxation of the longitudinal-optical (LO) phonons. The data are fit by an Einstein temperature for the LO phonons, $\Theta_{\mathrm{LO}}=650$ K, and a Grüneisen constant $\gamma_{\mathrm{LO}}=-3.4$. An unusually long phonon relaxation time is found.

Hydrogen in palladium hydride occupies the octahedral interstitial sites in the Pd fcc lattice. In the high-concentration, α', phase, more than 60% of the octahedral sites are filled.[1] Ultrasonic attenuation[2-4] and internal friction[5-8] peaks have been observed in α'-PdH$_x$ and attributed to a stress-induced rearrangement of the H atoms on the interstitial sites, a type of Zener relaxation attenuation. The present Rapid Communication reports the results of ultrasonic attenuation measurements in single-crystal α'-PdD$_x$. A Zener-type attenuation peak is observed, similar to the case for the hydride. Surprisingly, a second peak is observed in the deuteride which is not present in the hydride. This second peak has quite unusual properties and is the focus of the present paper. The peak is interpreted in terms of an interaction between the ultrasonic wave and the optical phonons associated with the deuterons.

Ultrasonic waves were propagated along the [110] axis in single-crystal PdD$_x$. Data were taken for $x=0.64$, 0.67, 0.69, and 0.72. Qualitatively similar results were obtained for all concentrations, but the most extensive data were taken for $x=0.67$ which is the case described below. The longitudinal and two independent transverse waves were investigated. The cylindrically shaped sample was approximately 0.71 cm long and 0.95 cm in diameter and was charged with deuterium by a process which avoided the mixed-phase region. Details of the sample preparation have been given previously.[2-4]

Figure 1 shows data for the ultrasonic attenuation of longitudinal waves propagating along the [110] direction. A temperature-independent background attenuation has been subtracted from the data. Two major attenuation peaks are evident. The peaks occurring in the neighborhood of 200 K are similar to those observed in PdH$_x$ and attributed to Zener relaxation. These peaks are not the subject of the present paper. For each frequency a second peak is observed at lower temperature. At 10.3 MHz this peak occurs at approximately 104 K and is approximately 0.2 dB/cm in magnitude. At 142 MHz the peak has shifted to approximately 140 K and is approximately 10 dB/cm in magnitude, an increase of a factor of 50 for a factor of 14 increase in frequency. Figure 2 shows data for the C' mode: ultrasonic waves propagating along [110], but polarized along [$\bar{1}$10]. The low-temperature peak is absent. A similar result was obtained for the other pure transverse mode: propagation along [110], but polarized along [001]. Finally, the low-temperature peak was never observed in PdH$_x$ for any of the three independent ultrasonic modes.

The shift in temperature with increasing frequency is characteristic of a relaxation process with a temperature-dependent relaxation time. The usual expression[2] for the amplitude attenuation coefficient α is (in units of Np/cm),

$$\alpha=\frac{\delta C}{C}\frac{\omega}{2v}\frac{\omega\tau}{1+\omega^2\tau^2}, \tag{1}$$

where $\omega/2\pi$ is the ultrasonic frequency, τ is the relaxation time, v is the ultrasonic velocity, and $\delta C/C$ is called the relaxation strength.

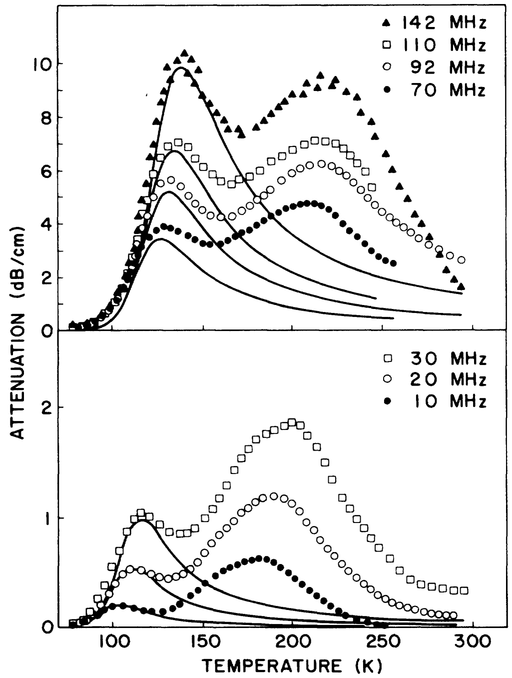

FIG. 1. Ultrasonic attenuation vs temperature in PdD$_{0.67}$ for longitudinal waves along [110] at various frequencies. The different symbols indicate the experimental data at different frequencies while the solid lines are a theoretical fit using $\Theta_{\mathrm{LO}}=650$ K, $\gamma_{\mathrm{LO}}=-3.4$, $\tau_0^{-1}=3.7\times10^{12}$ sec^{-1}, and $Q=93$ meV.

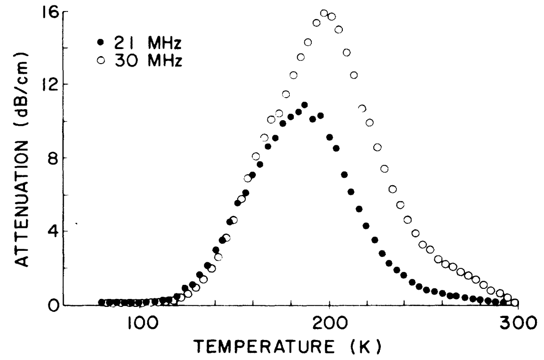

FIG. 2. Ultrasonic attenuation vs temperature in PdD$_{0.67}$ for transverse waves propagating along [110] and polarized along [$\bar{1}$10].

The low-temperature attenuation peaks have at least three unusual properties: (1) They are observed for longitudinal waves, but not transverse waves; (2) they are observed in PdD$_x$, but not in PdH$_x$; (3) interpreted as relaxation in terms of Eq. (1) it is found that *$\delta C/C$ increases* with increasing temperature whereas the usual case is that *$\delta C/C$ decreases* with increasing temperature.

We interpret the attenuation as arising from an interaction between the ultrasonic wave and the optical phonons associated with the D vibrations. The interaction of ultrasonic waves with thermal phonons has been reviewed by Maris.[9] There are two basic theoretical approaches to the problem. One method, due to Landau and Rumer,[10] is microscopic in nature. The ultrasonic wave is treated as a beam of phonons which interacts *via* energy-momentum-conserving collisions with the thermal phonons. Another method, due to Akheiser,[11] treats the ultrasonic wave macroscopically and a Boltzmann equation approach is used. Because of anharmonicities, the strain produced by the ultrasonic wave modulates the frequencies of the thermal phonons and hence their equilibrium populations. The phonon populations require a finite time τ to adjust to the new equilibrium conditions. The finite relaxation time leads to a relaxation-type attenuation of the ultrasonic wave. It was originally argued that the Boltzmann equation approach was only valid in the limit $\omega\tau \ll 1$, but Maris[9] has shown that the approach is valid for $\hbar\omega \ll kT$, a much less restrictive condition. A similar argument has been presented by Simons.[12] In general the problem of Akheiser damping is very complex because many different Grüneisen constants and relaxation times may be required to fully describe the various phonon branches. A single well-defined ultrasonic attenuation peak attributable to thermal phonon relaxation is not normally observed.

Of the many theoretical treatments[9] of ultrasonic attenuation due to interaction with thermal phonons, few have dealt explicitly with optical phonons. Barrett[13] used a Boltzmann equation approach to treat the optical phonons in KTaO$_3$. He used a simple model in which the phonons are treated as two groups described by γ_i, the Grüneisen constant for group i, τ_i, the relaxation time for group i, and C_i, the specific heat for group i. Although too simplified to fully describe the present situation, the two-group approach will be used as an approximate description. The attenuation in Np/cm is found to be

$$\alpha = \frac{\omega}{2\rho v^3}\frac{TC_1C_2}{C_1+C_2}(\gamma_1-\gamma_2)^2\frac{\omega\tau}{1+\omega^2\tau^2}\,, \tag{2a}$$

where

$$\tau = \frac{C_1\tau_2+C_2\tau_1}{C_1+C_2}\,, \tag{2b}$$

and T is the temperature.

An intuitively appealing approach is to take one group as all the acoustic phonons and the second group as all the optic phonons; however, we have not been able to find a fit to the data with reasonable values for the parameters using this approach. Rather, we make the following identification: Group 1 = all acoustic phonons + all *transverse*-optic phonons; group 2 = all *longitudinal*-optic phonons. (The values of the Grüneisen constants γ_{ac}, γ_{TO}, and γ_{LO} turn out to justify this identification.) Then we have $C_1 = C_{\mathrm{ac}} + C_{\mathrm{TO}}$. We use the Debye theory with $\Theta_D = 285$ K (Ref. 14) for C_{ac} and Einstein theory with $\Theta_{\mathrm{TO}} = 460$ K (40 meV) (Ref. 15) for C_{TO}. Then $C_2 = C_{\mathrm{LO}}$ where

$$C_{\mathrm{LO}} = \frac{Nkx}{V}\left(\frac{\Theta_{\mathrm{LO}}}{T}\right)^2\frac{\exp(\Theta_{\mathrm{LO}}/T)}{[\exp(\Theta_{\mathrm{LO}}/T)-1]^2}\,, \tag{3}$$

N/V being the number of Pd atoms per unit volume, k is Boltzmann's constant, x is the D/Pd ratio, and Θ_{LO} is the Einstein temperature for the longitudinal-optical phonons. For τ we use the convenient expression

$$\tau = \tau_0 \exp\left(\frac{Q}{kT}\right)\,. \tag{4}$$

The fitting parameters are then $|\gamma_1-\gamma_2|$, Θ_{LO}, τ_0, and Q.

Figure 1 shows that the high-temperature peak (Zener relaxation) overlaps the low-temperature peak. Although the argument is too long to present here, a detailed comparison of both longitudinal and transverse attenuation results on PdH$_{0.67}$ with corresponding results on PdD$_{0.67}$ indicates that the influence of the Zener peak on the low-temperature peak is negligible at temperatures *below the maximum* of the low-temperature peak. Thus we will only attempt to fit Eq. (2) to the experimental results for temperatures up to the maxima of the low-temperature peaks.

The solid lines in Fig. 1 show the fit to the data. A factor of 8.68 has been used to convert nepers to decibels. The agreement between theory and experiment is seen to be quite good for temperatures up to the maxima of the low-temperature peaks. We now turn to a discussion of the fitting parameters.

The peak shifts to higher temperatures as the frequency is increased because the condition $\omega\tau \approx 1$ must be met and τ depends on temperature. The *growth* of the maximum peak height with temperature is controlled largely by the temperature dependence of C_{LO} and hence by Θ_{LO}. We find $\Theta_{\mathrm{LO}} = 650$ K (56 meV) in excellent agreement with neutron scattering measurements for a maximum in the density of states of LO phonons.[16,17] It is this value which leads us to identify the effect with the LO phonons.

A value characteristic of the TO phonons does not give a good fit to the data.

The overall magnitude of the effect is largely determined by $|\gamma_l-\gamma_2|$. The fit to the data gives $|\gamma_l-\gamma_2|=6.8$. We compare this result with other measurements to determine a Grüneisen parameter for the LO phonons. From thermal expansion measurments Abbenseth and Wipf[18] find $\gamma_{ac}=3.0$ and $\gamma_0=3.0$ as overall Grüneisen constants for the acoustic and optic modes, respectively. Blascho, Burger, Klemencic, and Pepy[19] have measured mode Grüneisen parameters for a few transverse-optic phonons in $PdD_{0.71}$. They find $4\leq\gamma_{TO}\leq 6$. We take $\gamma_{TO}\approx 5$ and use these results to calculate γ_l. We find

$$\gamma_l=\frac{3C_{ac}+5C_{TO}}{C_{ac}+C_{TO}}\approx 3.4\,, \qquad (5)$$

over the temperature range of the fit. Combining this value of γ_l with $|\gamma_l-\gamma_2|=6.8$ from the fit we obtain $\gamma_{LO}=+10.2$, or -3.4. We choose the negative value to agree with the Abbenseth and Wipf thermal expansion data.

$$\gamma_0=\frac{5C_{TO}-3.4C_{LO}}{C_{TO}+C_{LO}}\approx 3.2\,, \qquad (6)$$

in excellent agreement with the value of 3.0 quoted above. Although the evidence was less direct than in the present case, a negative value for γ_{LO} was indicated[20,21] by an investigation of the elastic constants of PdH_x and PdD_x.

For the relaxation time we find $\tau_0^{-1}=3.7\times10^{12}$ sec^{-1}, and $Q=93$ meV. The relaxation time is quite long compared to that usually found for phonons, e.g., our results give $\tau\approx1\times10^{-8}$ s at $T=100$ K. This value is roughly three orders of magnitude longer than is typical for thermal phonons at this temperature.[9] It was shown by Orbach and Vredevoe[22] that conservation of energy and momentum severely limits three-phonon decay processes, and in certain cases very long phonon lifetimes were predicted. The dispersion curves[15,23] for PdD_x indicate that energy and momentum considerations will place strong constraints on phonon decay in this system. As an example, energy conservation alone prevents the decay of 56-meV LO phonons directly to acoustic phonons by a three-phonon process. It appears that decay to an LA and a TO phonon is possible, but only for a narrow range of the final states. Although the relaxation time was fit to an exponential temperature dependence, $\tau\propto T^{-9}$ would also fit the data. It is worth noting, however, that ultrasonic attenuation in rutile was interpreted in terms of an exponential temperature dependence for the relaxation of the optic phonons.[24] In addition, the paper by Orbach and Vredevoe gives theoretically an exponential temperature dependence for the relaxation of high-energy TA phonons. It is unclear which mode or modes possess the long relaxation times. In any case the very-high-energy optic phonons in metal hydrides, well separated from the acoustic modes, offer the possibility for unusual relaxation effects.

No attenuation peak was observed for transverse ultrasonic waves. However, transverse ultrasonic waves propagating along a high symmetry direction will give a *net* frequency shift of zero[13,20] for thermal phonons. For a particular $\mathbf{k}$ for which the ultrasonic strain is $+\epsilon$ there will be another wave vector $\mathbf{k}'$ ($k=k'$) related by symmetry for which the strain is $-\epsilon$. This effect is shown explicitly in the calculation of Mason and Batemann.[25] If intramode scattering is able to achieve thermal equilibrium in a time that is short compared to the period of the ultrasonic wave (e.g., LO phonons along [011] maintain thermal equilibrium with LO phonons along [10$\bar{1}$]), then there would be no attenuation due to intramode relaxation. Perhaps non-momentum-conserving elastic collisions with defects could maintain equilibrium. Since the *net* frequency shift of phonons of a particular type (e.g., LO phonons along [110] type directions) is zero, any effect involving relaxation between modes of different types, e.g., LO to LA, LO to TA, etc., would not be expected for pure transverse ultrasonic waves if thermal equilibrium is maintained within the mode.

The absence of an effect for the *hydride* is partially, but not completely, explained in terms of the higher vibrational frequency for H. The longitudinal Einstein temperature for the hydride is expected to be roughly $\sqrt{2}$ times that for the deuteride. When this higher value is used in Eqs. (2) and (3) the calculated attenuation is approximately five times lower for the hydride as compared to the deuteride. However, this lower value would still be observable. Apart from Θ_{LO} the other possible explanations for this isotope effect involve the Grüneisen constant and the relaxation time. The *overall* optic mode Grüneisen constant was found to be isotope independent.[18] If the relaxation in the hydride is faster than in the deuteride, $\omega\tau\approx1$ would occur at a lower temperature and the exponential dependence in Eq. (3) would ensure that the effect would be unobservable.

A novel ultrasonic attenuation peak has been observed in α'-PdD_x. Although the absence of the effect in PdH_x is not completely accounted for and the absence of an effect for transverse waves requires an assumption about thermal equilibrium, all other features of the peak are explained in terms of a redistribution of LO phonon populations in response to the ultrasonic wave. The Einstein temperature required to fit the data is in excellent agreement with neutron scattering results. A negative value is found for the Grüneisen parameter for the LO phonons. This result suggests unusual features for the potential experienced by the deuterons. The thermal phonon relaxation time required to fit the data is unusually long.

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