PHYSICAL REVIEW B VOLUME 20, NUMBER 4 15 AUGUST 1979

Elastic constants of palladium and β-phase palladium hydride between 4 and 300 K

D. K. Hsu and R. G. Leisure

Department of Physics, Colorado State University, Fort Collins, Colorado 80523

(Received 5 March 1979)

Elastic constants of palladium and palladium hydride in the β phase ($PdH_{0.66}$) have been measured on single-crystal samples in the temperature range of 4–300 K. The results obtained in palladium agree with previous measurements. The anomalous temperature dependence of the shear constant C_{44} in palladium is found to be absent in the hydride. The values of the adiabatic elastic constants C_{44}, $\frac{1}{2}(C_{11}-C_{12})$, and $\frac{1}{2}(C_{11}+C_{12}+2C_{44})$ in $PdH_{0.66}$ in units of 10^{12} dyne/cm^2 are, respectively, 0.691, 0.327, and 2.633 upon extrapolation to absolute zero. The Debye temperature of the hydride calculated from its elastic constants is 285 K at low temperature. The hydride elastic constants did not show any pronounced anomaly over the "50-K transition" temperature region.

I. INTRODUCTION

The elastic constants of transition metals are of considerable interest because they contain the contributions from both the lattice energy and the electron system.[1] The elastic constants of palladium have been the subject of several investigations[2–4] and the anomalous temperature dependence of the shear constants in palladium has been related to the temperature variation of the magnetic susceptibility of the metal.[5] It is well known that palladium absorbs hydrogen readily and the resulting hydride has many striking properties, including superconductivity at high hydrogen content[6] and a possible structural change at low temperatures (the so-called "50-K transition").[7,8] These properties have been of great interest in many recent studies. It is also established that the paramagnetism of palladium hydride[9] decreases linearly with increasing hydrogen content and the hydride becomes diamagnetic when the H to Pd atomic ratio reaches ~0.65. This should have a pronounced effect on the temperature dependence of the elastic constants of palladium hydride; however, the elastic constants of palladium hydride have not been measured before, possibly because of the difficulties with sample preparation. In fact, to our knowledge, the only acoustic-velocity measurements performed on metal hydrides were made by Beattie.[10] He used polycrystalline samples of the hydrides of Sc, Y, and Er and observed discontinuities of the temperature derivatives of the sound velocities which suggest some kind of phase transition in these hydrides. The objectives of this work were to make accurate measurements of the elastic constants, as a function of temperature, of palladium and palladium hydride on samples prepared from the same single crystal of palladium, to study the effects of the absorbed hydrogen, and to detect any anomaly which might be associated with the low-temperature transition of the hydride.

II. EXPERIMENTAL PROCEDURE

The samples of palladium and palladium hydride used in this work were prepared from a single crystal of palladium in the form of a cylindrical rod approximately 4 cm long and 1 cm in diameter obtained from Materials Research Corporation. The crystal was grown using the Czochralski method with its axis along the [110] crystalline direction and a chemical analysis showed the purity to be 99.98% with principal impurities being Pt, Fe, Cr, and C. The ingot was etched in HCl-HNO_3 (3:1 ratio) and its orientation was checked by x-ray back-reflection Laue photography to within 1 ° of the [110] direction. Two specimens, each of 1.2 cm length, were cut from the ingot with a low-speed diamond saw and the end faces were then polished flat and parallel. One of the specimens was used to obtain the elastic constant data for pure palladium and the other was subsequently hydrogenated.

The hydrogenation process was carried out by absorption from the gas phase in a pressure cell and furnace. In order to avoid the mixed $\alpha+\beta$ phase region and maintain the single crystallinity of the specimen, the sample was taken over the hump of the palladium hydride phase diagram[11] in the following steps: (i) the sample was first etched, cleaned, and weighed before loading into the pressure cell; (ii) the sample temperature was raised to 330 °C under vacuum and hydrogen gas was then introduced slowly. The pressure rose to 340 psi in about 8 hours; (iii) the sample was kept at 330 °C and under 340 psi hydrogen pressure for approximately 30 hours; and (iv) under the same hydrogen pressure, the temperature was lowered to ambient temperature in about 18 hours and finally the pressure was dropped to 1 atm and the sample removed from the cell. The hydrogen content was determined by the weight gain, and after an initial decrease of a few percent, was found to stabilize at a H to Pd ratio of 0.66 ± 0.02. The hydrogen content was checked periodically during the course of the experiments and no appreciable change was detected with the sample kept under ambient conditions for over one year. X-ray Laue photography taken from the as-hydrided sample surface showed a strain-free single-crystal pattern and an x-ray diffractometer scan on the same surface revealed a large (110) peak of the β phase with no observable α-phase peak. The single-crystal end faces were later polished, and subsequent x-ray diffraction investigations revealed no α phase and indicated a lattice parameter that is stable in time.

The elastic constants were determined from the sound velocities. The three pure modes of the longitudinal, the fast shear, and the slow shear waves were propagated along the [110] direction to obtain the elastic constants $\frac{1}{2}(C_{11}+C_{12}+C_{44})$, C_{44}, and $\frac{1}{2}(C_{11}-C_{12})$, respectively. The velocity measurements were made using a continuous-wave technique[12] in which mechanical standing-wave resonances were excited in the composite resonator consisting of the sample and the piezoelectric transducers. The velocity V was determined by measuring the frequency f_n of the nth mechanical resonance and is given by

$$V=\frac{2l_s f_n}{n}\left[1-\frac{2\rho_T l_T}{\rho_s l_s}\left(\frac{f_T-f_n}{f_n}\right)\right] ,$$

where

$$n=(f_n/\Delta f)(1-2\rho_T l_T/\rho_s l_s) .$$

In the above equation, l_s and l_T are the lengths of the sample and the transducer, respectively, and the corresponding densities are ρ_s and ρ_T. Δf is the frequency separation between adjacent mechanical resonances and f_T is the resonant frequency of the transducer. Frequency modulation and lock-in detection were used on the mechanical resonance chosen while the temperature was being changed slowly. The temperature was monitored with an Au + 0.07 at. % Fe and chromel thermocouple and a typical run from room temperature to liquid-helium temperature took 6 hours. Measurements were made at frequencies of 10, 20, and 60 MHz using X-cut and AC-cut quartz transducers. The Nonaq stopcock grease served as a satisfactory bonding agent down to liquid-helium temperature.

Thermal-expansion corrections must be made for the length and density of the sample in determining the sound velocity. For pure palladium, we have taken the lattice constant at 298 K to be 3.8900 Å,[13] which corresponds to a density of 12.01 g/cm^3 at the same temperature. The thermal-expansion data of Waterhouse and Yates,[14] and White and Pawlowicz[15] were used to correct both the length and the density of palladium.

The lattice constant of $PdH_{0.66}$ at room temperature was found to be 4.0287 Å by x-ray diffraction. A corresponding density of 10.84 g/cm^3 is calculated. (Water-displacement measurement gave a density slightly higher, 10.87 g/cm^3.) The thermal-expansion data of palladium hydride can not be found in the literature, except for the x-ray lattice parameter measurements by King and Manchester[16] on $PdH_{0.67}$ from liquid-helium to liquid-nitrogen temperature. We have used a DuPont thermomechanical analyzer to measure the thermal expansion of the palladium and $PdH_{0.66}$ crystals used in this work from room temperature to liquid-nitrogen temperature. The results on pure palladium are in reasonable agreement with published data and the results on $PdH_{0.66}$ show a somewhat larger $\Delta l/l$ from 300 to 77 K, 28.5×10^{-4}, than the corresponding value 22.8×10^{-4} of palladium. The thermal-expansion curve was extended to liquid-helium temperature using the lattice parameters of King and Manchester, and is used in the length and density corrections for sound velocity and elastic constant calculations.

Repeated measurements of the elastic constants on both samples usually reproduce to within 0.3% or better. The absolute accuracy of the elastic constants

TABLE I. Ultrasonic velocities in Pd and $PdH_{0.66}$ (units of 10^5 cm/sec).

	Pd		$PdH_{0.66}$	
	4 K	295 K	4 K	295 K
$\vec{q} \parallel [110]$ $\vec{\xi} \parallel [110]$	4.776	4.743	4.907	4.775
$\vec{q} \parallel [110]$ $\vec{\xi} \parallel [001]$	2.424	2.436	2.513	2.421
$\vec{q} \parallel [110]$ $\vec{\xi} \parallel [\bar{1}10]$	1.547	1.456	1.733	1.588

of $PdH_{0.66}$, depending on the accuracy of the density and thermal-expansion data, is estimated to be 1%.

Palladium has remarkably good acoustic properties among metals. The low attenuation allows sharp standing-wave resonances to be set up in the sample which facilitates the accurate measurement of sound velocity. We found that the hydrogenated sample $PdH_{0.66}$ is also excellent for acoustic propagation; for example, nearly 100 echoes can be seen when it is pulsed with 10 MHz longitudinal waves. Table I lists the ultrasonic velocities in Pd and $PdH_{0.66}$ at room temperature and liquid-helium temperature. The number of significant figures indicates the relative accuracy of the measurements.

III. RESULTS AND DISCUSSION

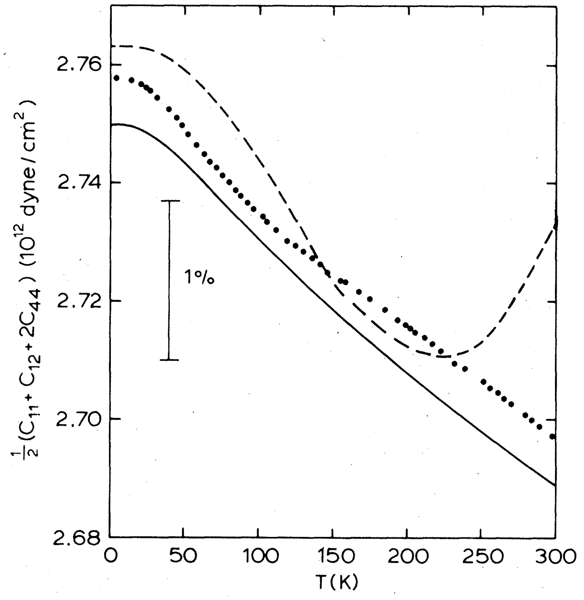

FIG. 1. Elastic constant $\frac{1}{2}(C_{11}+C_{12}+2C_{44})$ vs temperature in palladium. Results of this work are represented by dots. Previous measurements by Rayne (dashed line) and by Walker *et al.* (solid line) are replotted here for comparison.

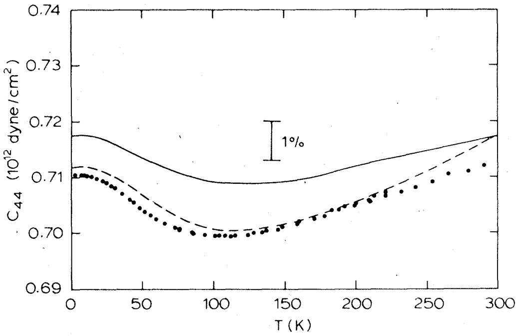

FIG. 2. Elastic constant C_{44} vs temperature in palladium. Results of this work are represented by dots. Previous measurements by Rayne (dashed line) and by Walker *et al.* (solid line) are replotted here for comparison.

Figures 1–3 show our results for the elastic constants of palladium, together with previous measurements of Rayne[2] and Walker *et al.*[3] Rayne's $\frac{1}{2}(C_{11}+C_{12}+2C_{44})$ data show a minimum at 220 K while both the results of Walker *et al.* and the present work give a monotonic temperature dependence with a slight positive curvature. Our data and the data of Walker *et al.* are in agreement to 0.4%. The shear constant $\frac{1}{2}(C_{11}-C_{12})$ of this work is in excellent agreement with both previous measurements and only our data are shown. As can be seen, $\frac{1}{2}(C_{11}-C_{12})$ also has a slight positive curvature. The shear constant C_{44} is of particular interest because all three measurements showed a minimum in the vicinity of 120 K. The present data agree with Rayne's results to 0.3% and are 1% lower than those obtained by Walker *et al.* Rayne interpreted the unusual temperature behavior of C_{44} in terms of the change with temperature of the contribution by the holes in the 4*d* band of palladium. Weinmann and Steinemann[5] proposed a model in which the temperature dependent C_{44} is written as the sum of an anharmonic term and a polarization term which is negative and contains the magnetic susceptibility χ. They showed that the minimum of C_{44} corresponds to the maximum of the susceptibility χ and their calculated

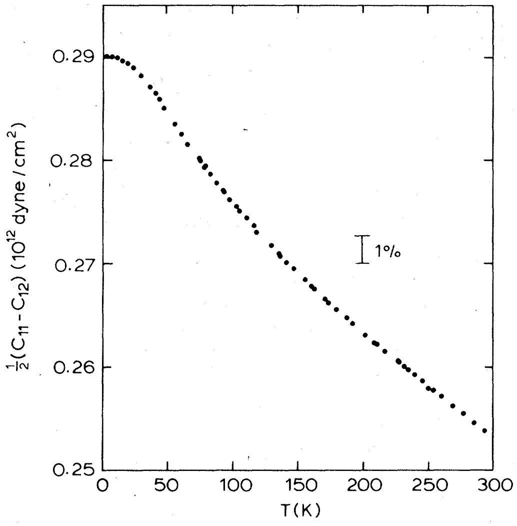

FIG. 3. Elastic constant $\frac{1}{2}(C_{11}-C_{12})$ vs temperature in palladium. Results of previous measurements by Rayne and by Walker *et al.* are identical to this work.

TABLE II. Elastic properties of palladium. The zero-temperature values are extrapolated from 4 K. The elastic constants are in units of 10^{12} dyne/cm^2. The number of significant figures indicates the sensitivity to temperature dependence, not the absolute accuracy. Bulk modulus $B=\frac{1}{3}(C_{11}+2C_{12})$ and anisotropy ratio $A=2C_{44}/(C_{11}-C_{12})$.

T (K)	C_{44}	$\frac{1}{2}(C_{11}-C_{12})$	$\frac{1}{2}(C_{11}+C_{12}+2C_{44})$	B	A
0	0.7105	0.2900	2.7577	1.9505	2.4500
20	0.7095	0.2894	2.7568	1.9508	2.4516
40	0.7063	0.2866	2.7522	1.9504	2.4644
60	0.7025	0.2828	2.7457	1.9489	2.4841
80	0.7003	0.2792	2.7400	1.9466	2.5082
100	0.6995	0.2760	2.7346	1.9431	2.5344
120	0.6995	0.2731	2.7302	1.9397	2.5613
140	0.7004	0.2704	2.7265	1.9360	2.5902
160	0.7018	0.2678	2.7225	1.9314	2.6206
180	0.7034	0.2655	2.7193	1.9274	2.6493
200	0.7050	0.2633	2.7157	1.9229	2.6776
220	0.7067	0.2612	2.7122	1.9184	2.7056
240	0.7082	0.2592	2.7085	1.9139	2.7323
260	0.7096	0.2570	2.7047	1.9094	2.7611
280	0.7111	0.2550	2.7008	1.9047	2.7886
300	0.7125	0.2533	2.6970	1.9001	2.8129

values of C_{44} are in good agreement with their measurement. Walker *et al.* have also measured the elastic constants of single-crystal Pd-Rh and Pd-Ag alloys and the minimum of C_{44} in pure palladium slowly disappeared upon alloying with Rh and Ag. Based on our measurements of the elastic constants, we have computed the bulk modulus $B=\frac{1}{3}(C_{11}+2C_{12})$ and the anisotropy ratio $A=2C_{44}/(C_{11}-C_{12})$ and the results are presented in Table II.

Figures 4–6 and Table III are the results of the elastic constant measurements in $PdH_{0.66}$ over the 4–300 K range. The following observations can be

TABLE III. Elastic properties of β-phase palladium hydride ($PdH_{0.66}$). The zero-temperature values are extrapolated from 4 K. The elastic constants are in units of 10^{12} dyne/cm^2. The number of significant figures indicates the sensitivity to temperature dependence, not the absolute accuracy. The bulk modulus $B=\frac{1}{3}(C_{11}+2C_{12})$ and the anisotropy ratio $A=2C_{44}/(C_{11}-C_{12})$.

T (K)	C_{44}	$\frac{1}{2}(C_{11}-C_{12})$	$\frac{1}{2}(C_{11}+C_{12}+2C_{44})$	B	A
0	0.6905	0.3278	2.6330	1.8332	2.1065
20	0.6905	0.3278	2.6330	1.8332	2.1065
40	0.6895	0.3265	2.6310	1.8327	2.1118
60	0.6877	0.3245	2.6272	1.8313	2.1193
80	0.6850	0.3218	2.6220	1.8297	2.1287
100	0.6820	0.3188	2.6145	1.8262	2.1393
120	0.6788	0.3153	2.6055	1.8216	2.1529
140	0.6750	0.3117	2.5950	1.8161	2.1655
160	0.6707	0.3072	2.5828	1.8097	2.1833
180	0.6660	0.3023	2.5682	1.8014	2.2031
200	0.6610	0.2969	2.5520	1.7920	2.2263
220	0.6560	0.2910	2.5360	1.7830	2.2543
240	0.6506	0.2858	2.5200	1.7741	2.2764
260	0.6454	0.2807	2.5030	1.7640	2.2993
280	0.6398	0.2760	2.4862	1.7544	2.3181
300	0.6345	0.2713	2.4720	1.7471	2.3387

made: (i) Figures 4–6 show quite normal behavior for the elastic constants with no evidence of the type of anomaly observed in the C_{44} of pure palladium. The elastic constants have the usual linear high-temperature behavior expected from anharmonic theory and approach absolute zero with a zero slope. Based on the model of Weinmann and Steinemann,[5] the absence of an anomaly is expected due to the fact that the magnetic susceptibility[9] of the hydride has decreased to zero at the H to Pd concentration ratio of 0.66.

(ii) The elastic constants obtained from all three pure acoustic modes along the [110] direction show a negative curvature or concavity toward the temperature axis. It is noted that the elastic constants of the hydride approach a linear temperature dependence at a relatively high temperature (~180 K), although the Debye temperature of $PdH_{0.66}$ is comparable to metals such as silver, gold, and tantalum where the elastic constants are essentially linear above 50 K or so.

(iii) Both C_{44} and $\frac{1}{2}(C_{11}+C_{12}+2C_{44})$ of the hydride are lower than their corresponding values in palladium whereas the value of $\frac{1}{2}(C_{11}-C_{12})$ in the hydride is considerably higher than that in palladium. This effect is not yet understood.

(iv) We have investigated the power-law behavior of the hydride elastic constant in the 4–180 K range by plotting the logarithm of the changes in the elastic constants, $C(T)-C(0)$, versus ln T. The resulting curves suggest a fairly close T^4 dependence at low temperatures and T^2 dependence at higher temperatures with a somewhat sharp kink around 50 K. This change takes place at a temperature which suggests that it might be associated with the "50-K transition" temperature. However, all the elastic constants are

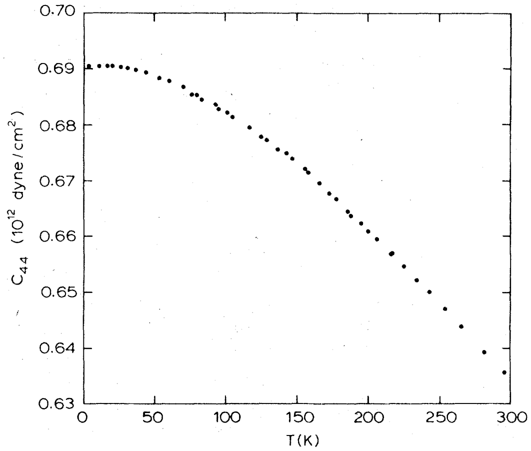

FIG. 5. Elastic constant C_{44} vs temperature in $PdH_{0.66}$.

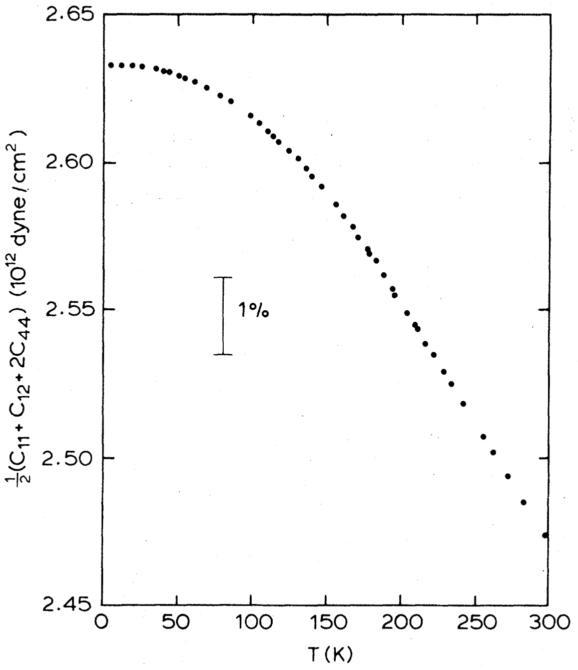

FIG. 4. Elastic constant $\frac{1}{2}(C_{11}+C_{12}+2C_{44})$ vs temperature in $PdH_{0.66}$.

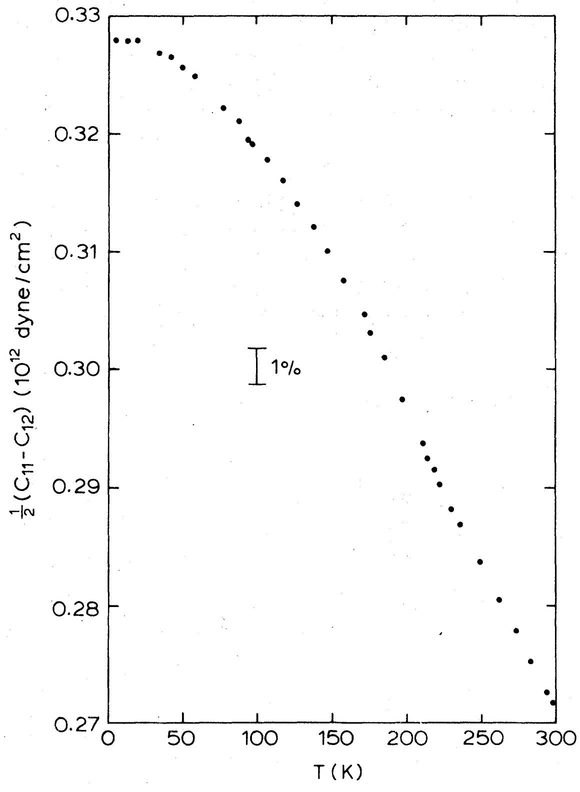

FIG. 6. Elastic constant $\frac{1}{2}(C_{11}-C_{12})$ vs temperature in $PdH_{0.66}$.

changing rather smoothly over that temperature range, indicating no pronounced structure change of the hydride is taking place. Based on the elastic constant data, we can not rule out any sharp structural transformation which may have a very small velocity anomaly (of the order 1 part in 10^3 or less) taking place over a narrow temperature range.

(v) The athermal values of the elastic constants are obtained by extrapolating the linear region to absolute zero temperature and the results in units of 10^{12} dyne/cm^2 are as follows: $C_{44}=0.715$, $\frac{1}{2}(C_{11}-C_{12})=2.716$, and $\frac{1}{2}(C_{11}+C_{12}+2C_{44})=0.350$. These values are to be compared with a harmonic theory of the lattice with no zero-point vibrations.

The Debye temperature in the low-temperature limit, Θ_0, can be computed from the elastic constants. deLaunay[17] has shown that

$$\Theta_0 = \left(\frac{9N}{4\pi V}\right)^{1/3}\left(\frac{h}{k}\right)\left(\frac{C_{44}}{\rho_s}\right)^{1/2}\left(\frac{9f}{18+3^{1/2}}\right)^{1/3},$$

where h is the Planck constant, k is the Boltzmann constant, and f is a function of the factors s and t, which, in the central force model with electron-gas modification, are given by

$$s=\frac{C_{11}-C_{44}}{C_{12}+C_{44}},\quad t=\frac{C_{12}-C_{44}}{C_{44}} .$$

Using the table of deLaunay, we obtained a value of $f=0.655$. Taking $N/V=6.2\times10^{22}$ cm^{-3} as the number of palladium atoms per unit volume of $PdH_{0.66}$ and $\rho_s=10.94$ g/cm^3 as its density extrapolated to zero temperature, we computed a value of Θ_0 to be 285 K. As a check of this value, we have also used the graphical method of Marcus[18] where Θ_0 is given by

$$\Theta_0 = \left(\frac{h}{k}\right)\left(\frac{3N}{4\pi V}\right)^{1/3}\left(\frac{C_{11}}{\rho_s}\right)^{1/2} g$$

and the numerical value of g, a function of ratios of the elastic constants, is found to be 0.53 by using the graphs of Marcus. Using this value, we again obtained $\Theta_0=285$ K. The uncertainty in the obtained Debye temperature, depending largely on the value of the density used, is estimated to be ±3 K. The Debye temperature of $PdH_{0.66}$ is approximately 10° higher than that of pure palladium. Our pure palladium elastic constants gave a Θ_0 of 276 K, which agrees well with Rayne's value of 275 ± 8 K.

In conclusion, we have measured the elastic constants of Pd and $PdH_{0.66}$ from room temperature down to liquid-helium temperature. The temperature dependence of the $PdH_{0.66}$ elastic constants is markedly different from that of palladium and can be understood in terms of the magnetic susceptibility of the hydride. The hydride elastic constants showed no unusual behavior near 50 K, the temperature where anomalies in electrical resistivity, specific heat, and internal friction have been observed. However, a small change in the sound velocity occuring over a narrow temperature range has not been ruled out by this measurement. In contrast to the pronounced changes in temperature derivatives of the sound velocities observed in polycrystalline hydrides of Sc, Y and Er,[10] the behavior of the palladium hydride elastic constants is more normal.

ACKNOWLEDGMENTS

This work is supported by a grant from Research Corporation. The authors gratefully acknowledge Dr. Charles Lundin and Dr. Frank Lynch of the Denver Research Institute for hydrogenating some of our samples and Professor F. D. Manchester for sending us Ref. 16 prior to its publication.

---

[1] O. Fischer, M. Peter, and S. Steinemann, Helv. Phys. Acta 42, 459 (1969).

[2] J. A. Rayne, Phys. Rev. 118, 1545 (1960).

[3] E. Walker, J. Ortelli, and M. Peter, Phys. Lett. A 31, 240 (1970).

[4] C. Weinmann and S. Steinemann, Phys. Lett. A 47, 275 (1974).

[5] C. Weinmann and S. Steinemann, Solid State Commun. 15, 281 (1974).

[6] T. Skoskiewicz, Phys. Status Solidi A 11, K123 (1972); B. Stritzker and W. Buckel, Z. Phys. 257, 1 (1972).

[7] J. K. Jacobs and F. D. Manchester, J. Less-Common Metals 49, 67 (1976).

[8] T. Ellis, C. B. Satterthwaite, M. Mueller, T. O. Brun, and H. Knott, Bull. Am. Phys. Soc. 23, 235 (1978).

[9] F. A. Lewis, *The Palladium Hydrogen System* (Academic, New York, 1967).

[10] A. G. Beattie, J. Appl. Phys. 43, 3219 (1972).

[11] A method first used by F. D. Manchester. See, for example, J. K. Jacobs, C. R. Brown, V. S. Pavlov, and F. D. Manchester, J. Phys. F 6, 2219 (1976).

[12] R. G. Leisure and R. W. Moss, Rev. Sci. Instrum. 40, 946 (1969).

[13] S. V. Nagender Naidu and C. R. Houska, J. Appl. Phys. 42, 4971 (1971).

[14] N. Waterhouse and B. Yates, Cryogenics 8, 267 (1968).

[15] G. K. White and A. T. Pawlowicz, J. Low Temp. Phys. 2, 631 (1970).

[16] H. W. King and F. D. Manchester, J. Phys. F 8, 15 (1978).

[17] J. deLaunay, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1956), Vol. 2.

[18] G. A. Alers, in *Physical Acoustics*, edited by W. P. Mason (Academic, New York, 1965), Vol. III B.