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Brief Reports

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Elastic constants of α'-phase PdH_x over the temperature range 4–300 K

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The elastic constants of α'-phase PdH_x have been determined from ultrasonic velocity measurements for x up to 0.76 over the temperature range 4–300 K. For pure Pd and $PdH_{0.67}$ the results are in good agreement with earlier measurements. The $PdH_{0.76}$ data are for a higher hydrogen concentration than has previously been reported. The low-temperature concentration dependences of the Debye temperature and bulk modulus are given.

INTRODUCTION

The understanding of metal hydrides continues to improve as the results from many different experimental techniques become available. There is a continuing need for accurate data for many different physical quantities for well-characterized systems over a wide range of hydrogen concentration. We report here new results for the elastic constants of a metal hydride. The elastic constants of solids are related to interatomic forces and are thus of fundamental interest. In addition, elastic properties are related to thermal properties through the Debye theory. Finally, elastic properties such as the bulk modulus are needed for the calculation of many thermodynamic quantities.

The elastic constants of palladium hydride were first given for $PdH_{0.66}$ by Hsu and Leisure.[1] There have since been other reports[2,3] of elastic constants of PdH_x with x as high as 0.73. We report here results for PdH_x for $x = 0$, 0.67, and 0.76, over the temperature range 4–300 K. The present results extend our knowledge of the hydrogen concentration dependence of the elastic constants, bulk modulus, and Debye temperature for this system.

EXPERIMENTAL DETAILS

The cylindrical ingot from which the PdH_x sample was cut was purchased from Metal Crystals and Oxides Ltd. (U.K.). The crystal was grown from Johnson Matthey Grade 1 material assayed as 99.998% pure. A sample approximately 1 cm in diameter and 0.75 cm long was cut from the single-crystal ingot using a low-speed diamond saw. The crystalline orientation was determined by x-ray back-reflection Laue photography and then the end faces of the samples were polished flat and parallel in preparation for ultrasonic measurements. The end faces of the sample were perpendicular to the [110] direction to within 1°. After cutting and polishing the sample was annealed in vacuum at 800 °C for 1 h.

Charging with hydrogen was done in a pressure cell and furnace by a process which avoided the mixed phase region. One PdH_x sample was prepared by charging along a 500 °C isotherm up to a hydrogen pressure of 41 atm. The temperature and pressure were then lowered in such a way as to keep the sample well outside the mixed phase region. The resulting hydride had a hydrogen concentration of 0.72. Hydrogen was allowed to evolve at room temperature until the concentration reached 0.67, at which point the measurements were made. The sample was stored in liquid nitrogen when not being used in the experiment to prevent escape of the hydrogen. After a series of ultrasonic measurements were made the hydrogen was removed, again by avoiding the mixed phase region. To a sensitivity of 2×10^{-5} the weight of the sample before and after loading and unloading the hydrogen was the same. This crystal was next charged along a 500 °C isotherm to a hydrogen pressure of 68 atm. After bringing the temperature and pressure to the ambient values the hydrogen concentration was 0.764.

In each case the charging time was approximately 100 h and the temperature and pressure were changed in timed intervals to avoid concentration gradients larger than 1%. The final concentration was determined by weight gain.

The 0.764 sample was treated with a KI solution to poison the surface and slow the escape of hydrogen. This treatment has a negligible effect on the weight of the sample. Next, the sample was electroplated with a copper film approximately 22 μm thick. Careful records were kept of the weight of the sample using a microbalance with a resolution of 0.1 mg. After the measurements were finished the copper film was removed. Within the sensitivity of the microbalance the weight of the sample just before copper plating and just after removal of the film was the same. Some hydrogen escaped before the poisoning operation so that the hydrogen concentration during the ultrasonic measurements was 0.760.

The elastic constants were calculated from the sound velocities. The longitudinal and two independent transverse modes were propagated along the [110] crystalline direction. The relations between the sound velocities v and the elastic constants C_{ij} are

$$\rho v_l^2 = \tfrac{1}{2}(C_{11} + C_{12} + 2C_{44}) = C_L \ , \tag{1a}$$

$$\rho v_{t_1}^2 = C_{44} = C \ , \tag{1b}$$

$$\rho v_{t_2}^2 = \tfrac{1}{2}(C_{11} - C_{12}) = C' \ , \tag{1c}$$

where v_l denotes longitudinal waves, v_{t_1} and v_{t_2} correspond to sound waves polarized along the [001] and [$\bar{1}$10] directions, respectively, and ρ is the sample density. The sound velocities were measured with a continuous-wave technique.[1,4,5] Standing-wave resonances were excited in a composite resonator consisting of sample, transducers on each end face, and, in the case of the high-concentration sample, copper films. Consecutive standing-wave resonance frequencies were measured over a frequency range around 10 MHz. Corrections were applied to the data to account for the effect of the transducers and copper films on the measured resonant frequencies.[4]

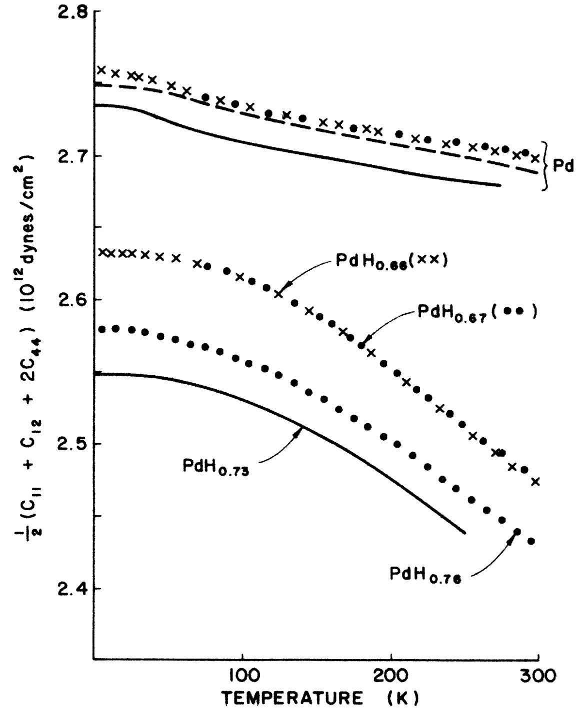

FIG. 1. Elastic constant C_L vs temperature. The present results are given by the solid circles, the ×'s represent the data of Hsu and Leisure (Ref. 1), the solid line represents the data of Geerken *et al.* (Ref. 3), while the dashed line represents the data of Walker *et al.* (Ref. 8).

Densities were measured[6] at room temperature for each sample, using a fluid displacement method. The thermal expansion data of Hemmes *et al.*[7] were used to calculate the low-temperature density and sample length from the room-temperature values. Ultrasonic velocity data were collected on lowering the temperature from room temperature with a maximum rate of change of 1 K/min.

RESULTS AND DISCUSSION

Our measurements, along with previous results, are given in Figs. 1–3. The elastic constants of pure Pd were measured from room temperature down to liquid-nitrogen temperature in the present study. Although the single crystal used in the present work was obtained from an independent source, the present results are virtually identical to the earlier data of Hsu and Leisure,[1] and are also in reasonable agreement with other data.[3,8] We find also that the present results for $PdH_{0.67}$ are in very good agreement with the earlier data for $Pd_{0.66}$ from room temperature down to liquid-nitrogen temperature. Finally, we present results for $PdH_{0.76}$. As was found in the earlier ultrasonic[1–3] studies, the elastic constants C_L and C_{44} decrease on going from pure Pd to the high-concentration, α', phase, while C' increases. These results are consistent with neutron scattering results[9,10] in the long-wavelength limit. The present results show that

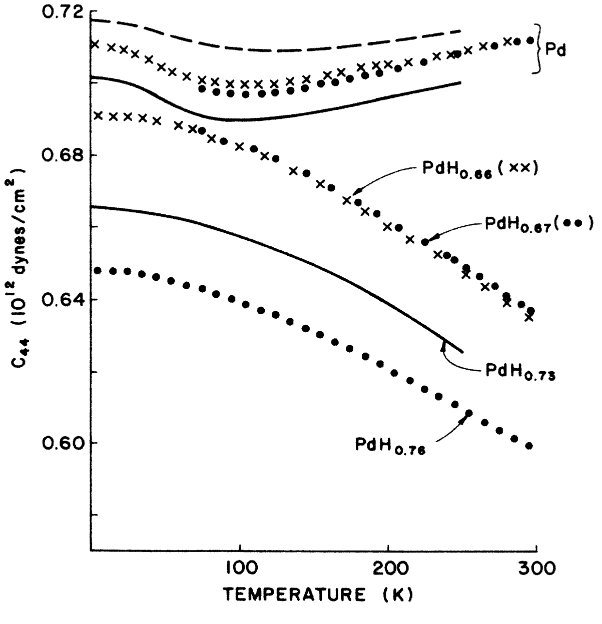

FIG. 2. Elastic constant C_{44} vs temperature. The symbols are the same as for Fig. 1.

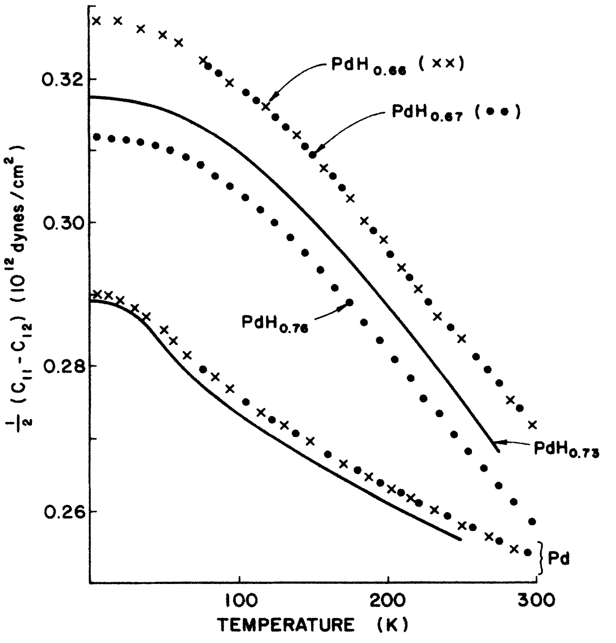

FIG. 3. Elastic constant C' vs temperature. The symbols are the same as for Fig. 1.

all three elastic constants decrease with increasing H concentration in the α'phase. Our data and those Geerken *et al.*[3] are in remarkable agreement for the α'-phase concentration dependence of C_{44} and C', but disagree somewhat for C_L. Overall, however, the agreement between the two sets of data is quite good. It has been pointed out[3] that in a central force model with only first- and second-neighbor interactions,[11] C' is especially sensitive to second-neighbor interactions. The behavior of the elastic constants on going from pure Pd to the α'-phase PdH$_x$ was attributed to a softening of the first-neighbor force constants due to an expansion of the lattice, but a hardening of the second-neighbor Pd-Pd force constant due to H occupation of the interstitial site between second-neighbor Pd atoms. A simple interpretation of that model is that C' would continue to harden as the H concentration is increased in the α' phase. In contrast, the present results show that all three elastic constants soften in the α' phase as the concentration is increased.

The elastic constants provide information about the nature of the interatomic forces. If central forces are operative and the crystal has an inversion center the Cauchy relations apply. These relations reduce to $C_{44}=C_{12}$ for cubic crystals. The ratio C_{44}/C_{12} is given in Table I for a temperature of 4 K. The Cauchy relation is strongly violated with no marked concentration dependence.

We have also calculated the low-temperature bulk modulus from our data. The results are given in Table I. The bulk modulus decreases on going from pure Pd to PdH$_{0.66}$, but within the estimated accuracy of the experiments remains constant in the α' phase.

TABLE I. The bulk modulus B, the anisotropy ratio A, C_{44}/C_{12}, and the Debye temperature at a temperature of 4 K for pure Pd, PdH$_{0.66}$, and PdH$_{0.76}$. B is in units of 10^{12} dyn/cm^2.

	B	A	C_{44}/C_{12}	Θ (K)
Pd	1.95	2.45	0.404	276
PdH$_{0.66}$	1.83	2.11	0.424	283
PdH$_{0.76}$	1.83	2.08	0.400	278

Also given in Table I is the anisotropy ratio $A=C_{44}/C'$. The anisotropy ratio decreases steadily with increasing H concentration.

Finally, we use the 4-K elastic constants to calculate the Debye temperature in the low-temperature limit. deLaunay has shown that[12]

$$\Theta=\left[\frac{9N}{4\pi V}\right]^{1/3}\frac{h}{k}\left[\frac{C_{44}}{\rho}\right]^{1/2}\left[\frac{9f}{18+3^{1/2}}\right]^{1/3}, \tag{2}$$

where h and k are Planck's and Boltzmann's constants, respectively, ρ is the hydride density, N/V is the number of Pd atoms per unit volume of PdH$_x$, and f is a function of the factors s and t, which in the central force model with an electron gas modification, are given by

$$s=\frac{C_{11}-C_{44}}{C_{12}+C_{44}}, \quad t=\frac{C_{12}-C_{44}}{C_{44}}. \tag{3}$$

We have also used the method of Marcus[13] to calculate Θ from the elastic constants. The two methods gave the same value of Θ to within 0.5 K. The results are given in Table I.

There has been inconsistency in the literature in the interpretation of N/V for hydrides.[14,15] An excellent discussion of the various contributions to the heat capacity of metal hydrides has recently been given by Moss *et al.*[16] Taking Θ to represent the acoustic contribution to the heat capacity, N/V is just the number of Pd atoms per unit volume; the hydrogen atoms are not counted. Of course, the hydrogen atoms affect the acoustic terms indirectly through the elastic constants C_{ij} and the density ρ.

Accurate values have been given for the elastic constants of carefully prepared Pd and PdH$_x$ single crystals. Low-temperature values of certain elastic properties and the Debye temperature have been tabulated. The various physical quantities related to the elastic energy and acoustic excitations may now be calculated more accurately and at a higher hydrogen concentration than previously possible.

ACKNOWLEDGMENT

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