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Isotope effects and pressure dependence of the T_c of superconducting stoichiometric PdH and PdD synthesized and measured in a diamond anvil cell

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We have synthesized stoichiometric PdH and PdD in a diamond anvil cell and measured *in situ* the pressure dependence of the superconducting transition temperature. From an analysis of the results and band-structure calculations, we find that both the anharmonicity of the Pd-H potential and the effect of the large zero-point motion of the hydrogen isotopes are needed to explain the inverse isotope effect and the observed pressure dependence of T_c .

I. INTRODUCTION

Shortly after the discovery of superconductivity in palladium hydrides by Skoskiewicz,¹ an isotope effect in T_c was found by Stritzker and Buckel.² Contrary to the expectations from a simple BCS theory the T_c of Pd-D was higher than that of Pd-H. Recently Schirber *et al.*³ measured an even larger inverse isotope effect for Pd-T.

Several mechanisms have been proposed to explain this inverse isotope effect, including anharmonicity of the Pd-H potential⁴ and electronic effects resulting from the large zero-point motion (zpm) of the hydrogen,⁵ which both affect the electron-phonon coupling parameter. Papaconstantopoulos *et al.*^{6,7} combined band structure calculations for the electronic part (η) and neutron-scattering results for the phonon part ($M\omega^2$) of the electron-phonon coupling parameter (λ). They concluded that the isotope effect was the result of the anharmonicity of the Pd-H potential only. However, Griessen and de Groot⁸ showed on the basis of thermal expansion, bulk modulus and point-contact spectroscopy data that anharmonic effects in Pd-H and Pd-D are a factor 2 smaller than was assumed by Papaconstantopoulos *et al.*,⁷ and thus is insufficient to explain the observed isotope effect. This conclusion was recently confirmed by new neutron-scattering data on palladium hydrogen by Rush *et al.*⁹ and on palladium tritium (PdT_{0.7}) by Rowe *et al.*¹⁰

Recently Jena *et al.*,¹¹ following an idea of Miller and Satterthwaite,⁵ calculated the effect of the zpm on the electronic part ($\eta_{H(D)}$) of the electron-phonon coupling parameter for hydrogen (deuterium). They calculated the electron scattering for several deviations of the H(D) atom from the equilibrium position and determined an average $\eta_{H(D)}$. The resulting isotope effect in $\eta_{H(D)}$ was, however, too small to explain the isotope effect (see also the discussion in Ref. 10). A different approach was taken by Karakozov and Maksimov¹² and by Griessen and de Groot⁸ who proposed that the $\eta_{H(D)}$, determined from band structure calculations, should be multiplied by a

atoms. The Debye-Waller factor can be neglected for most superconductors since the mean-square displacement of the atoms is small. For hydrogen in Pd-H the zpm is, however, so large that the Debye-Waller factor has to be included. Griessen and de Groot⁸ showed that the anharmonicity and the isotope dependence of the Debye-Waller factor are sufficient to explain the inverse isotope effect in T_c . Zhernov and Drekhslers,¹³ however, arrived at a smaller Debye-Waller factor and suggested that Coulomb and spin-paramagnon interactions could play an important role.

As it is difficult to check the validity of a theory by comparing only one parameter, the calculated T_c , with experimental data we decided to investigate the pressure dependence of T_c of PdH and PdD. In order to avoid complications with the interpretation, the experimental conditions were chosen in such a way that the samples were stoichiometric.

When loading a metal with hydrogen, the hydrogen concentration is determined by the thermodynamic equilibrium condition $\mu_H(x, P, T) = \frac{1}{2}\mu_{H_2}(P, T)$. Here μ_H is the chemical potential of the hydrogen in the metal at a hydrogen concentration x and μ_{H_2} is the chemical potential of the molecular hydrogen surrounding the metal, both at a pressure P and temperature T . In general the hydrogen concentration increases with the hydrogen pressure. For a more detailed account of the thermodynamics metal-hydride formation see Refs. 14 and 15.

Palladium-hydride samples with $x \approx 1$ can be obtained at high hydrogen pressures. From the results given by Driessen *et al.*¹⁴ and the thermodynamic properties of hydrogen at high pressures from Hemmes *et al.*¹⁶ we estimate that, at $T = 100$ K and $P = 30$ kbar, it is possible to synthesize PdH _{x} with $x \approx 0.999$. This can be considered stoichiometric for the purpose of the present work.

In order to study the pressure dependence of the T_c of PdH, we had to develop a new technique for the synthesis of stoichiometric metal hydrides in a high pressure cell.

II. EXPERIMENTAL

We describe here the technique used to load metal samples at high pressures with hydrogen in a diamond anvil cell (DAC) and to make *in situ* resistance measurements. Our DAC is similar to that of Silvera and Wijngaarden.¹⁷ The DAC, which is entirely made of a BeCu alloy (Berylco 25), is mounted in an optical cryostat for use in the temperature range 2–300 K. The body of the cell contains a heat exchanger, which can be operated with liquid helium. With this we can cool the cell rapidly to liquid helium temperatures. The force on the diamonds can be changed continuously at all temperatures from outside the cryostat. Details of the DAC and the cryogenic system are given elsewhere.¹⁸ The pressure is measured using the standard ruby fluorescence technique and the pressure scale of Mao *et al.*¹⁹

In the course of the experiment the metal sample is always surrounded by hydrogen under high pressure. Because of the large compressibility of hydrogen the sample volume is loaded with liquid hydrogen which has a sufficient high density for further compression in the DAC. To achieve this we built a small chamber around the diamond tips, as shown in Fig. 1. The diamonds are mounted in brass rings using an epoxy resin. The resin also prevents leaking of the chamber. The chamber is closed by a teflon seal around the brass rings. The hydrogen is introduced in gaseous form using a capillary which enters the chamber through the teflon seal. When filling the chamber with gaseous hydrogen the DAC is at a temperature just above the triple point of hydrogen (~ 14 K) so that the gas entering the chamber condenses.

The electrical leads for the resistance measurements enter the chamber through channels that are drilled in one of the brass rings (see Fig. 1). The channels are sealed with epoxy resin to keep the chamber leak tight.

In our experiments we used eight-sided diamonds without bevels and a culet of 1.2 mm diameter and 16-sided diamonds with bevels of 0.2 mm under an angle of 5° and a culet of 0.8 mm diameter.

It is very difficult to make contacts to samples of the size typically used in DAC experiments ($\sim 100 \times 100 \times 10 \mu\text{m}^3$). Therefore we used another approach. We evaporated a thin film ($\sim 0.1 \mu\text{m}$ thick) of Pd on the culet of one of the diamonds and used photolithographic techniques to pattern the Pd film. One of the patterns used is shown in Fig. 2. The electrical contacts to the sample are incorporated in the pattern. They go all the way to the

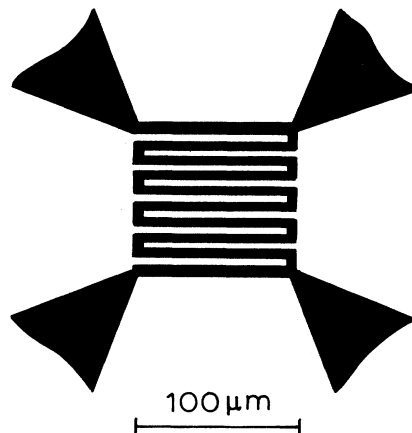


FIG. 2. Patterned Pd film on one of the diamonds, used to measure the resistance of the sample. The wedge formed shapes on the corners form the electrical contacts and extend to the edge of the culet.

edge of the culet. Using an ultrasonic thermobonding technique we connect Au wires with a diameter of $25 \mu\text{m}$ to the pattern. The Au contacts are placed near the edge of the culet. They do not enter the sample volume defined by the hole in the gasket, which is $\sim 300 \mu\text{m}$ in diameter at the start of the experiment. Contact between the Au wires and the electrical leads, which enter the chamber through the channels in the brass ring, is made on the side of the diamond using a conducting glue. The sample and the gold contacts are electrically insulated from the gasket by a $25 \mu\text{m}$ thick poly-Imide foil (Kapton). The insulator has a $300 \mu\text{m}$ large hole at the position of the sample space in the gasket. More details can be found in Ref. 20.

In a typical run we follow the procedure described below. After assembly, the DAC is cooled down to the triple temperature of hydrogen (or deuterium). There has to be a gap between one of the diamonds and the gasket (as shown in Fig. 1) to allow the condensed hydrogen to fill the sample space. This process can be monitored through the diamonds and the windows of the cryostat, using a microscope combined with a video camera. As soon as the sample space is filled with liquid hydrogen sufficient force is applied to the diamonds to bring them together and seal the sample space.

At the low temperatures where the sample space is filled with hydrogen, the diffusion of the hydrogen into the Pd is negligible. To load the Pd with hydrogen we have thus to increase the temperature. The loading of the Pd film is monitored by measuring its resistance. In Fig. 3 we show the resistance of the sample when the DAC is warmed up with 2 K/min . At first we see an increase in resistance due to the thermally induced electron-phonon scattering in pure Pd. Above $\sim 110 \text{ K}$, where the loading of the Pd with hydrogen starts, we see a strong increase in the resistance as a result of the disordered distribution of the hydrogen on the interstitial lattice, which causes a strong electron scattering.²¹ When the hydride approaches stoichiometry the disorder on the

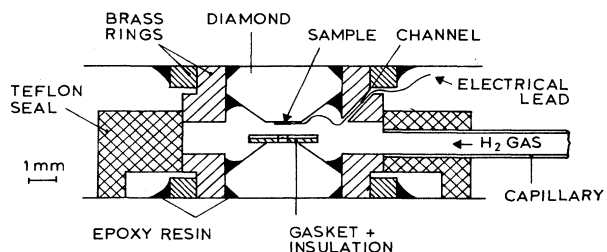


FIG. 1. Cross section of the construction around the diamonds. For details see text.

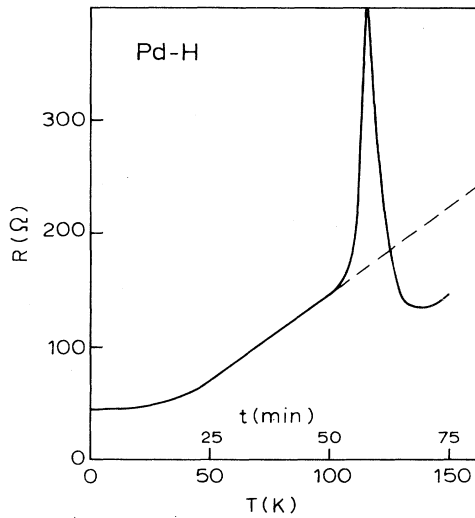


FIG. 3. Resistance of the sample during the loading with hydrogen. The resistance was measured while heating the DAC at a rate of 2 K/min. The hydrogen absorption starts at ~ 110 K, as can be seen from the strong increase in resistance. When approaching stoichiometry the resistance reduces again. Note that the resistance of PdH is then significantly lower than that of pure Pd.

interstitial lattice is reduced and the resistance decreases again. As a consequence the resistance shows a maximum as can be seen in Fig. 3. Since the loading of the sample takes place during the heating of the DAC, the height and the width of the peak in Fig. 3 depend on the heating rate. When the hydrogen concentration in the Pd gets in equilibrium with the hydrogen outside the Pd at the given temperature and pressure, the increase in electron-phonon scattering with temperature will dominate again over the change due to the electron-disorder scattering. We see this as an upturn in the resistance in Fig. 3. At this point we can cool down again and start the measurements on the pressure dependence of the superconducting transition temperature of the sample.

At pressures of ~ 35 kbar and temperatures of ~ 120 K we have synthesized stoichiometric PdH and PdD. We have measured the pressure dependence of the T_c of PdH and PdD between 0 and ~ 40 kbar. Typical transitions at several pressures are shown in Fig. 4. The small widths of the transitions indicate that the sample is loaded homogeneously with hydrogen. From an extrapolation to zero pressure we found $T_c = 8.80$ K for PdH and $T_c = 11.05$ K for PdD, in agreement with data available from literature.²² The pressure dependence of the T_c of PdH and PdD is shown in Fig. 5. The points are the 50% values of the transitions and the width of the transitions is indicated by the vertical bars. The uncertainty in the pressure determination is ~ 0.7 kbar. From the experimental data we find a logarithmic pressure dependence $\partial \ln T_c / \partial P = -6.8 \times 10^{-3} \text{ kbar}^{-1}$ for PdH and $\partial \ln T_c / \partial P = -5.0 \times 10^{-3} \text{ kbar}^{-1}$. To compare these results with theory we convert first the pressure depen-

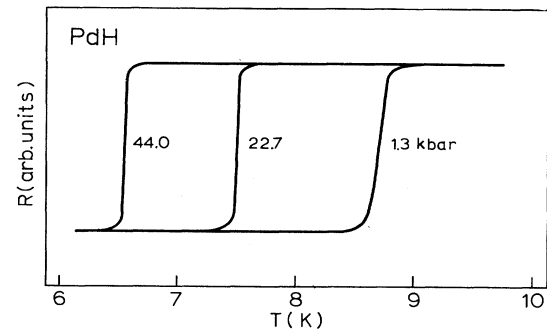


FIG. 4. Superconducting transitions in the resistance of PdH at three pressures.

dence of T_c into a volume derivative.

If we have a sample under hydrostatic compression, the relation between the pressure and volume dependence of T_c is given by

$$\frac{\partial \ln T_c}{\partial P} = -\frac{1}{B} \frac{\partial \ln T_c}{\partial \ln V}, \quad (1)$$

where $B = -V \partial P / \partial V$ is the bulk modulus. In our experiments the sample is a film which is fixed with one side to the diamond surface. The lateral dimensions of the sample (10–100 μm) are much larger than its thickness ($\sim 0.1 \mu\text{m}$). Therefore even when a hydrostatic pressure P is applied, the film is essentially strained uniaxially. In this case the volume change of a cubic crystal (such as PdH and PdD) is not determined by the bulk modulus B , but by an effective elastic modulus B' (Ref. 23)

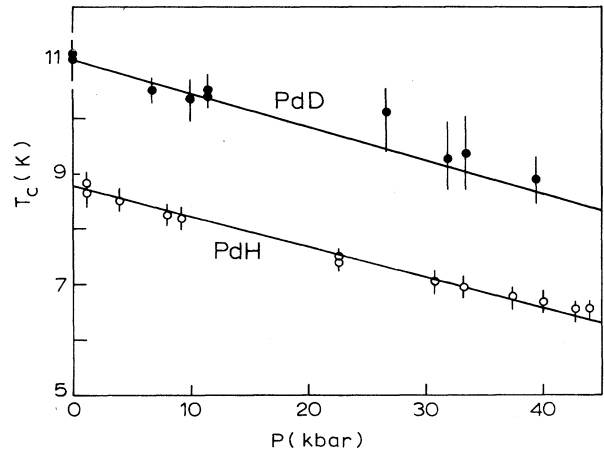


FIG. 5. Pressure dependence of the superconducting transition temperature of PdH and PdD. The symbols give the middle and the vertical bars give the width of the transitions. The theoretical results are given by the drawn curves. They are calculated with $\Theta_{\text{Pd}} = 230$ K, $\Theta_{\text{H}} = 728$ K, $\Theta_{\text{D}} = 485$ K, $\lambda_{\text{Pd}} = 0.175$, $\lambda_{\text{H}} = 0.3734$, $\lambda_{\text{D}} = 0.4680$, $\gamma_{\text{Pd}}^{\text{v}} = 2.5$, $\gamma_{\text{H}}^{\text{v}} = \gamma_{\text{D}}^{\text{v}} = 3.5$, $\gamma_{\text{Pd}}^{\text{f}} = 3.4$, $\gamma_{\text{H}}^{\text{f}} = \gamma_{\text{D}}^{\text{f}} = -1.22$, $\gamma_{\text{H}}^{\text{f}} = 0.88$, $\gamma_{\text{D}}^{\text{f}} = 0.66$, $\mu^* = 0.085$, $a = 4.09$ Å, and $B' = 2.11$ Mbar.

$$B' = B3 \frac{1-\sigma}{1+\sigma}, \quad (2)$$

where σ is Poisson's ratio. For the experimental situation chosen in this work the bulk modulus in Eq. (1) has thus to be replaced by B' defined in Eq. (2). To calculate B' we need the bulk modulus and Poisson's ratio for PdH and PdD. For this we extrapolated the data of Geerken *et al.*²⁴ on the concentration dependence of the elastic constants of substoichiometric PdH_x and PdD_x. We found $B=1.60$ Mbar and $\sigma=0.39$ and from Eq. (2) $B'=2.11$ Mbar. For the experimental volume dependence of T_c we find then $\partial \ln T_c / \partial \ln V = 14.4$ for PdH and $\partial \ln T_c / \partial \ln V = 10.6$ for PdD.

Until now we have not discussed the effect of elastic boundary conditions on the volume expansion accompanying the loading of the sample with hydrogen. From measurements of the pressure-composition isotherms of Pd films evaporated on quartz substrates²⁵⁻²⁷ we know, however, that the sticking of the film to the substrate decreases the temperature of the critical point somewhat but does not lead to a reduction of the maximum hydrogen content of the film. For example, the isotherms measured by Feenstra on 3000 Å thick films showed no significant deviations from those of bulk PdH_c.

Furthermore, in high pressure experiments on the Pd-Ag-H(D) system²⁸ we also measured on a free sample. The difference in pressure dependence of T_c between fixed and free samples is well explained by the renormalization of the bulk modulus discussed above.

The above strongly suggests that nonhydrostatic strains have a negligible influence on the superconducting properties of palladium hydrides(deuterides).

III. THEORY

In the first subsection we discuss the superconducting transition temperature and its pressure dependence. Then we present the band-structure calculations from which the electronic part (η) of the electron-phonon coupling parameter (λ) is determined.

A. Superconductivity

For the analysis of the results on the superconducting transition temperature we start with the Allen and Dynes²⁹ modification of McMillan's³⁰ T_c formula

$$T_c = \frac{\omega_{\log}}{1.20} \exp \left[-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right], \quad (3)$$

where ω_{\log} is a logarithmic average of the phonon frequencies, λ the electron-phonon coupling parameter, and μ^* the Coulomb pseudopotential. We neglect strong coupling correction factors since we are not in the strong coupling limit. Klein and Papaconstantopoulos³¹ showed that in the case of the Pd-H(D) system, where the mass of the metal atom is much larger than that of hydrogen, λ can be written as the sum of contributions from Pd and H(D), i.e.,

$$\lambda = \lambda_{\text{Pd}} + \lambda_{\text{H(D)}}, \quad (4)$$

where λ_{κ} can be written as^{30,31}

$$\lambda_{\kappa} = \eta_{\kappa} / (M_{\kappa} \omega_{\kappa}^2) \quad [\kappa = \text{Pd, H(D)}]. \quad (5)$$

The "electronic" parts (η_{κ}) of λ can be determined from band-structure calculations.^{30,32} The effect of the large zpm of hydrogen (deuterium) on $\eta_{\text{H(D)}}$ is not taken into account in these calculations. To incorporate the zpm, Griessen and de Groot⁸ proposed that $\eta_{\text{H(D)}}$ should be multiplied by a Debye-Waller factor $f_{\text{H(D)}}$ so that,

$$\lambda_{\text{H(D)}} = \eta_{\text{H(D)}} f_{\text{H(D)}} / (M_{\text{H(D)}} \omega_{\text{H(D)}}^2). \quad (6)$$

This factor reduces the electron-phonon coupling strength. Taking the logarithmic volume derivative of Eq. (3), we find

$$\frac{\partial \ln T_c}{\partial \ln V} = -\gamma_{\log} + g(\lambda) \frac{\partial \ln \lambda}{\partial \ln V} \quad (7)$$

with $\gamma_{\log} = -\partial \ln \omega_{\log} / \partial \ln V$ and

$$g(\lambda) = 1.04\lambda(1+0.38\mu^*) / [\lambda - \mu^*(1+0.62\lambda)]^2.$$

We have taken μ^* constant since we expect it to have only a small volume dependence compared to that of λ . Using Eq. (4), the volume dependence of λ can be expressed as

$$\frac{\partial \ln \lambda}{\partial \ln V} = \frac{\lambda_{\text{Pd}}}{\lambda} \frac{\partial \ln \lambda_{\text{Pd}}}{\partial \ln V} + \frac{\lambda_{\text{H(D)}}}{\lambda} \frac{\partial \ln \lambda_{\text{H(D)}}}{\partial \ln V}. \quad (8)$$

From Eqs. (5) and (6) we find for the volume dependence of λ_{Pd} and $\lambda_{\text{H(D)}}$:

$$\frac{\partial \ln \lambda_{\text{Pd}}}{\partial \ln V} = 2\gamma_{\text{Pd}}^{\omega} - \gamma_{\text{Pd}}^{\eta}, \quad (9a)$$

$$\frac{\partial \ln \lambda_{\text{H(D)}}}{\partial \ln V} = 2\gamma_{\text{H(D)}}^{\omega} - \gamma_{\text{H(D)}}^{\eta} - \gamma_{\text{H(D)}}^f, \quad (9b)$$

where the γ 's are defined by

$$2\gamma_{\kappa}^{\omega} = - \frac{\partial \ln M_{\kappa} \omega_{\kappa}^2}{\partial \ln V} \quad (10a)$$

$$\gamma_{\kappa}^{\eta} = - \frac{\partial \ln \eta_{\kappa}}{\partial \ln V} \quad (10b)$$

$$\gamma_{\text{H(D)}}^f = - \frac{\partial \ln f_{\text{H(D)}}}{\partial \ln V}, \quad (10c)$$

All parameters appearing in Eqs. (7)–(10) are available from literature or can be calculated.

In order to determine the necessary average phonon frequencies, we need the phonon density of states (PDOS) $F(\omega)$. Because of the large mass difference of the atoms, the acoustic and the optic modes are well separated. We use a Debye spectrum for the acoustic modes and an Einstein spectrum for the optic modes due to the Pd and H(D) atoms, respectively. We then have $F(\omega) = F_{\text{ac}}(\omega) + F_{\text{opt}}(\omega)$, with

$$F_{\text{ac}} = 3\omega^2 / \omega_{\text{ac}}^3 \quad (0 \leq \omega \leq \omega_{\text{ac}}, \text{ zero elsewhere}), \quad (11a)$$

$$F_{\text{opt}} = \delta(\omega - \omega_{\text{opt}}) \quad (\omega = \omega_{\text{opt}}, \text{ zero elsewhere}), \quad (11b)$$

where ω_{ac} is the Debye frequency of the acoustic modes associated with the Pd vibrations and ω_{opt} the Einstein frequency of the optic modes associated with the hydrogen (deuterium) vibrations.

This approximate PDOS is justified, as far as our application is concerned, because the frequency moments of our model PDOS agree very well with those obtained from experimental phonon spectra.^{10,33} Using our model PDOS and a generalization of McMillan's "constant α^2 " approximation^{30,31} we can calculate ω_{log} [see Eq. (3)] analytically, and we obtain

$$\omega_{\text{log}} = \omega_{\text{ac}}^{(\lambda_{\text{ac}}/\lambda)} \omega_{\text{opt}}^{(\lambda_{\text{opt}}/\lambda)} \exp(-\lambda_{\text{ac}}/2\lambda). \quad (12)$$

Here λ_{ac} and λ_{opt} correspond to λ_{Pd} and $\lambda_{\text{H(D)}}$, respectively, and $\lambda = \lambda_{\text{ac}} + \lambda_{\text{opt}}$. Using Eq. (11) we can also calculate the mean-square frequencies ω_{κ}^2 in Eqs. (5) and (6).

B. Band-structure calculations

In order to study the influence of pressure on the electronic part of the electron-phonon coupling constant λ of PdH and PdD we have performed augmented plane wave band-structure calculations for two different lattice constants. The electronic structure (at zero pressure) of many metal hydrides have been reviewed recently by Gupta and Schlappbach.³⁴ The lattice parameter for the uncompressed state is the same as used by Papaconstantopoulos *et al.*⁷ and Gupta and Freeman.³¹ The two calculations have been carried out following the same procedure as used by Gupta and Freeman.³¹ For the construction of the crystal potential the Slater local exchange approximation was used and departures of the potential from a constant value in the interstitial region, the so-called warped muffin-tin corrections,³⁵ have been included. Since our goal was to focus on the variation of the electronic part of the electron-optical phonon coupling, we carefully treated the H sites in the same manner for the two lattice parameters by using the same muffin-tin radius for the H spheres. From the energy eigenvalues generated *ab initio* at 89 points in the irreducible $\frac{1}{48}$ wedge of the Brillouin zone, the densities of states (DOS) have been accurately obtained using the linear-energy tetrahedron integration scheme³⁶ with 6048 micro tetrahedra in the fcc Brillouin zone.

We have then evaluated the electronic parts η_{Pd} and $\eta_{\text{H(D)}}$ of the electron-phonon coupling constant λ using the formulation proposed by Gaspari and Gyorffy,³² which is based on the rigid ion approximation. These authors have shown that for each atomic site κ [$\kappa = \text{Pd, H(D)}$], η_{κ} can be conveniently expressed in terms of quantities obtained from band-structure calculations

$$\eta_{\kappa} = N(E_F) \langle I_{\kappa}^2 \rangle = \frac{E_F}{N^*(E_F) \pi^2} \sum_l 2(l+1) \sin^2(\delta_{l+1}^{\kappa} - \delta_l^{\kappa}) \times \frac{n_l^{\kappa} n_{l+1}^{\kappa}}{n_l^{\kappa(1)} n_{l+1}^{\kappa(1)}}, \quad (13)$$

where δ_l^{κ} is the phase shift of angular momentum charac-

ter l of the potential at site κ , n_l^{κ} and $n_l^{\kappa(1)}$ are, respectively, the DOS and the free scatterer DOS of angular momentum character l at site κ , $N^*(E_F)$ is the total DOS for one spin direction, and $N(E_F)$ is the total DOS for both spin directions. All quantities are calculated at the Fermi energy E_F .

In the rest of this section we first give the results of the band-structure calculations and then the results for the electronic parts of the electron-phonon coupling parameter.

1. Electronic structure

A comparison between the energy bands and densities of states obtained from the calculations at two lattice parameters can be briefly summarized as follows. Upon compression of the lattice ($\Delta a/a = -0.02$), the transition metal d -band width (measured from L_1 to X_5) increased by 10.6%, while the low-energy metal-hydrogen bonding band width increases only by 5.5%. This behavior is consistent with the a^{-5} dependence³⁷ usually assumed for the tight-binding metal d - d and the a^{-2} dependence³⁸ for the metal- d hydrogen- s interaction parameters which govern, respectively, the d -band width and the metal-hydrogen bonding band width.

Upon compression of the lattice, the crystal field splitting at Γ between the metal d states of t_{2g} and e_g symmetry (from Γ'_{25} to Γ_{12}) increases by 12%. The increased metal-hydrogen interaction leads to a 6.2% lowering of the center of the metal-hydrogen bonding band, relative to the Fermi level position. As the band widths increase, the total density of occupied states decrease. On compression, the total DOS at the Fermi energy $N(E_F)$ decreases by 7.4% from the value of 6.81 states per Rydberg-unit cell ($a = 4.090$ Å) to 6.306 states per Rydberg-unit cell ($a = 4.008$ Å). The Fermi level of the hydride with reduced lattice constant lies at higher energy relative to the top of the d band, hence the energy difference between X_5 , which marks the top of the flat dispersed parts of the d bands, and E_F increases by about 3.9%. This feature has consequences for the character of the states at the Fermi energy and for the value of the "electronic" contribution η of the electron-phonon coupling constant. A list of the changes in some of the relevant energy differences in the band structure is shown in Table I.

2. Electron-phonon coupling

The hydrogen potential scatters strongly s waves and it has been observed that for all the metal hydrides, the s ($l=0$) scattering phase shift δ_0^H at the Fermi energy is always close to a resonance ($\delta_0^H \sim \pi/2$). The phase shifts of higher angular momentum components at the H site are very small. Consequently the value of η_H is dominated by the s - p scattering mechanism.²⁹ From the results listed in Table II we see that as the lattice is compressed, δ_0^H decreases since the Fermi level lies at higher energies. The ratios of the partial DOS of s and p type at the H site to the total DOS value increase. In particular, the larger p component obtained under pressure at the H site results

TABLE I. Energy differences (in Rydberg) in the band structure of PdH(D) for two lattice constants.

Position	$a=4.090 \text{ \AA}$	$a=4.008 \text{ \AA}$	
L_1-X_5	0.317	0.3507	d -band width
$\Gamma_1-L'_2$	0.313	0.3303	width of low energy band
$\Gamma_{25}-\Gamma_{12}$	0.077	0.0863	$t_{2g}-e_g$ crystal-field splitting
X_5-E_F	0.039	0.0405	position of E_F above the top of the d bands
	0.5565	0.5909	center of the low-energy band relative to E_F

from a stronger overlap with the tails of the d wave functions of the neighboring Pd atoms having a p symmetry at the H sites. This increase of n_s/N and n_p/N is compensated by a concomittent increase of the free scatterer densities of state $n_l^{(1)}$ which appear in the denominator of Eq. (11). The increase of $n_l^{(1)}$ can be understood in terms of a greater localization of the s and p wave functions inside the muffin-tin spheres since the Fermi level has been shifted upwards and lies in a region of the bands where the anti bonding character of the wave functions is larger.

Due to the interplay of the different terms, the value of $\eta_H = N(E_F) \langle I_H^2 \rangle$ is found to decrease by 7.2% as $\Delta a/a$ decreases by 2%. This decrease is almost equal to the decrease of 7.4% found in $N(E_F)$, the total DOS at E_F , while the value of the matrix element $\langle I_H^2 \rangle$ remains almost constant.

From the results listed in Table II we can see that at the metal site the s and p scattering phase shifts are negative. This indicates a repulsive character of the metal potential for the s - and p -waves due to orthogonalization conditions to the corresponding core states. The d -wave phase shifts at E_F are positive and large, close to the value of π . In transition metals, the d wave phase shifts are known to increase with the filling of the metal d bands. We notice that δ_2^{Pd} is smaller for the compressed

PdH(D) lattice. This is due to the broadening of the metal d bands and results in a 27% increase in the $\sin^2(\delta_2^{\text{Pd}} - \delta_3^{\text{Pd}})$ term. The increase in the \sin^2 term combined with the 7.4% decrease in the total DOS leads to a $\sim 20\%$ increase in the value of η_{Pd} . Other terms in Eq. (13) show little variation.

The variation of η_{Pd} under compression is consistent with previous observations in metal hydrides. Similar calculations show a decrease in the value of η_{metal} from the pure metal to the hydride, which has been mostly ascribed to a decrease in the metal d - d interaction due to lattice expansion.³⁹

From the preceding we can determine the logarithmic volume dependence of the electronic parts of the electron-phonon interaction as defined in Eq. (10b). We find $\gamma_{\text{Pd}}^{\eta} = 3.4$ and $\gamma_H^{\eta} = \gamma_D^{\eta} = -1.22$.

IV. DISCUSSION

In this section we first discuss the isotope dependence of T_c at zero pressure. Then we discuss the pressure dependence of T_c and finally our results are compared with the pressure dependence of the T_c of substoichiometric palladium hydrides (deuterides).

TABLE II. Phase shifts, densities of states and electronic parts of the electron-phonon coupling parameter for the Pd and H(D) site and two lattice constants.

	$a=4.090 \text{ \AA}$		$a=4.008 \text{ \AA}$	
	Pd site	H site	Pd site	H site
	Phase shifts in radians			
δ_0	-0.5115	1.1931	-0.6053	1.1537
δ_1	-0.1094	0.0280	-0.1508	0.0359
δ_2	2.8066	0.006	2.7613	0.001
δ_3	0.0030	0.0	0.0932	0.4865
	Partial and total DOS at E_F in states of both spin per Ryd-unit-cell			
n_0	0.116	0.510	0.0932	0.4865
n_1	0.326	0.058	0.2627	0.0808
n_2	5.236	0.0032	4.796	0.0056
n_3	0.024	0.002	0.0203	0.0035
$N(E_F)$	6.81		6.306	
	Electronic part of electron-phonon coupling			
$\eta \text{ (eV \AA}^{-2}\text{)}$	0.886	0.641	1.063	0.595

A. T_c of PdH and PdD at zero pressure

To calculate T_c we need the phonon frequencies, the Debye-Waller factors, and the electronic parts (η_{Pd} and $\eta_{\text{H(D)}}$) of the electron-phonon coupling parameter for stoichiometric PdH and PdD. The η 's are already calculated for a stoichiometric composition.

The phonon frequencies have only been determined for substoichiometric hydrides. Geerken *et al.*²⁴ observed that the phonon frequencies of the optical modes, as determined from neutron-scattering experiments, are virtually independent of the hydrogen (deuterium) concentration. Using the phonon frequency moments of PdH and PdD determined by Rowe *et al.*,¹⁰ we find for the Einstein temperatures of the optical modes $\Theta_{\text{H}}=728$ K in PdH and $\Theta_{\text{D}}=485$ K in PdD. Furthermore the acoustic phonon frequencies decrease because the lattice expands on hydrogenation. Extrapolation of the Debye temperature to a stoichiometric composition gives $\Theta_{\text{Pd}}=230$ K.

In the case of stoichiometric PdH(D) the Fermi surface³⁴ is similar to that of copper but has larger necks at the [111] faces of the Brillouin zone. Umklapp processes which give the major contribution to $\eta_{\text{H(D)}}$ will therefore involve mainly K_{200} reciprocal lattice vectors. On the basis of these properties Griessen and de Groot⁸ proposed, as a rough approximation, that the Debye-Waller factor is given by $f_{\text{H(D)}} \simeq \exp(-\frac{1}{3}K_{200}^2 \langle u_{\text{H(D)}}^2 \rangle)$ which can be written as

$$f_{\text{H(D)}} \simeq \exp \left[-\frac{8\pi^2 \hbar^2}{a^2 M_{\text{H(D)}} \hbar \omega_{\text{H(D)}}} \right], \quad (14)$$

where $M_{\text{H(D)}}$ is the mass and $\omega_{\text{H(D)}}$ the Einstein frequency of the hydrogen (deuterium) atoms and a is the lattice parameter. Using the phonon energies corresponding to the Einstein temperatures mentioned above and the lattice parameter $a=4.09$ Å we find an isotope effect of $\sim 8\%$ in the Debye-Waller factor.

Using the phonon frequencies, the calculated η 's for the uncompressed lattice from Table II and the Debye-Waller factors $f_{\text{H}}=0.732$ and $f_{\text{D}}=0.791$ we can calculate λ_{Pd} , $\lambda_{\text{H(D)}}$, and ω_{log} for PdH and PdD. We take $\mu^*=0.085$, obtained from the Benneman and Garland formula for μ^* (Ref. 40) and the calculated DOS at the Fermi level, to calculate T_c with Eq. (3). The values we find are too large. If we use the values of η from Ref. 7, the T_c 's we find are too small. This is due to the fact that the values of $\eta_{\text{H(D)}}$ determined from band-structure calculations depend strongly on the details of the calculations and show a considerable spread (see Refs. 6, 7, 11, and this work). The value of η_{Pd} depends much less on the details of the calculations. In the remaining part of this work we therefore take the average of the available η values, $\bar{\eta}_{\text{Pd}}=0.876$ and $\bar{\eta}_{\text{H}}=\bar{\eta}_{\text{D}}=0.485$. With the same phonon data and Debye-Waller factors as above we get $\lambda_{\text{Pd}}=0.175$, $\lambda_{\text{H}}=0.377$, $\lambda_{\text{D}}=0.459$, $\omega_{\text{log}}=431$ K for PdH and $\omega_{\text{log}}=344$ K for PdD. With $\mu^*=0.085$ we find then $T_c=9.0$ K for PdH and $T_c=10.6$ K for PdD, in reasonable agreement with the experimental data (see Fig. 5).

B. Pressure dependence of the T_c of PdH and PdD

In order to calculate the volume dependence of T_c we do not only need the phonon frequencies, the Debye-Waller factors and the η 's, but also their volume dependencies, defined by Eqs. (7)–(10).

The volume dependence of the phonon frequencies, given by Gruneisen parameters $\gamma_{\text{H(D)}}^{\omega}$ and $\gamma_{\text{H(D)}}^{\omega_{\text{log}}}$, has been determined from thermal expansion measurements by Hemmes *et al.*⁴¹ They found $\gamma_{\text{Pd}}^{\omega}=2.5$ and $\gamma_{\text{H(D)}}^{\omega}=3.5$. The experiments were done on hydrides and deuterides with concentrations ranging from 0.63 to 0.76. Within the experimental accuracy $\gamma_{\text{H}}^{\omega}=\gamma_{\text{D}}^{\omega}$ and $\gamma_{\text{Pd}}^{\omega}$ and $\gamma_{\text{H(D)}}^{\omega}$ are concentration independent. The phonon frequencies were also obtained from the thermal expansion data. They found $\Theta_{\text{Pd}}=270$ K, $\Theta_{\text{H}}=720$ K, and $\Theta_{\text{D}}=480$ K, in excellent agreement with the neutron-scattering results.

The volume dependence of the Debye-Waller factor can be determined directly by differentiating Eq. (14). We find $\gamma_{\text{H}}^f=0.88$ and $\gamma_{\text{D}}^f=0.66$.

γ_{log} , given in Eq. (7), is approximately given by a weighted average of the phonon Gruneisen parameters $\gamma_{\text{Pd}}^{\omega}$ and $\gamma_{\text{H}}^{\omega}=\gamma_{\text{D}}^{\omega}$: $\gamma_{\text{log}} \simeq (\lambda_{\text{Pd}} \gamma_{\text{Pd}}^{\omega} + \lambda_{\text{H(D)}} \gamma_{\text{H(D)}}^{\omega}) / \lambda$. We obtain $\gamma_{\text{log}} \simeq 3.2$ for both PdH and PdD.

The volume dependence of the η 's is obtained above from the calculated η 's for two different lattice parameters: $\gamma_{\text{Pd}}^{\eta}=3.4$ and $\gamma_{\text{H}}^{\eta}=\gamma_{\text{D}}^{\eta}=-1.22$. This means that under compression η_{Pd} increases and $\eta_{\text{H(D)}}$ decreases.

Now we have all the quantities to calculate the volume dependence of T_c , using Eqs. (7)–(10). We find $\partial \ln T_c / \partial \ln V = 13.9$ for PdH and $\partial \ln T_c / \partial \ln V = 12.0$ for PdD, in good agreement with the experimental results ($\partial \ln T_c / \partial \ln V = 14.4$ for PdH and $\partial \ln T_c / \partial \ln V = 10.6$ for PdD).

Using Eqs. (7)–(10) and the parameters determined above we have calculated the pressure dependence of the T_c of PdH and PdD. The results are shown in Fig. 5 as the drawn lines. To get the correct T_c at zero pressure we used optimized values for the optical contributions to the electron-phonon parameter: $\lambda_{\text{H}}=0.373$ and $\lambda_{\text{D}}=0.468$. This gives us a volume dependence of T_c at zero pressure of $\partial \ln T_c / \partial \ln V = 14.0$ for PdH and $\partial \ln T_c / \partial \ln V = 11.7$ for PdD, close to the values obtained above.

Finally, it is interesting to point out that the contribution of the Pd atoms to the volume dependence of the electronic parts of the electron-phonon coupling parameter in $\partial \ln T_c / \partial \ln V$ practically cancels that of the H(D)-atoms, i.e., $\gamma_{\text{H(D)}}^{\eta} \lambda_{\text{H(D)}} + \gamma_{\text{Pd}}^{\eta} \lambda_{\text{Pd}} \simeq 0$ in Eq. (8). As a result the volume dependence of T_c is entirely determined by the volume dependence of the phonon frequencies in λ_{Pd} , $\lambda_{\text{H(D)}}$ and ω_{log} .

C. Pressure dependence of the T_c for substoichiometric Pd-H(D)

Until now we have only considered the pressure dependence of the T_c of stoichiometric PdH and PdD. However in the past there have been reports on the pressure dependence of the T_c of substoichiometric palladium hy-

driles.⁴²⁻⁴⁵ In Fig. 6 we have plotted $\partial \ln T_c / \partial P$ against T_c at zero pressure for several concentrations. Here we use T_c as a measure for the hydrogen (deuterium) concentration. Our results are in agreement with those obtained by Schirber *et al.*⁴² and Wühl⁴³ at lower T_c 's.

For random alloys as PdH_x we cannot determine the pressure dependence of T_c as above since no reliable means are presently available to calculate the concentration dependence of the electronic parts of the electron-phonon coupling parameter and their volume dependencies. However, as the quantity that depends strongest on the hydrogen (deuterium) concentration is $\eta_{\text{H(D)}}$ (and possibly $\gamma_{\text{H(D)}}^{\eta}$) we shall estimate $\eta_{\text{H(D)}}$ from T_c by means by Eq. (3).

Because of the small concentration range in which the palladium hydrides are superconducting we can take most of the parameters entering T_c and $\partial \ln T_c / \partial P$ to be concentration independent. Keeping Θ_{Pd} , $\Theta_{\text{H(D)}}$, μ^* , and λ_{Pd} constant, we use Eq. (3) and the experimental T_c to define an implicit equation from which $\lambda_{\text{H(D)}}$ can be determined.

To calculate $\partial \ln T_c / \partial P$ we take the bulk modulus B , γ^{ω} , and γ^f concentration independent. The electronic structure determining η_{Pd} is not very sensitive to the hydrogen concentration, so we keep $\gamma_{\text{Pd}}^{\eta}$ constant for $x \gtrsim 0.8$.

The case of $\gamma_{\text{H(D)}}^{\eta}$ is somewhat different. $\eta_{\text{H(D)}}$ itself is strongly concentration dependent. The volume dependence of $\eta_{\text{H(D)}}$ is governed by the change in position of the Fermi level with respect to the top of the d band. This influences the character of the states at the Fermi energy and through that the value of $\eta_{\text{H(D)}}$. Since their electronic structures are very similar we expect very similar volume dependencies of $\eta_{\text{H(D)}}$ for stoichiometric and substoichiometric $\text{PdH}_x(\text{D}_x)$. Because of this and because the volume dependence of $\eta_{\text{H(D)}}$ is much weaker than its concentration dependence, we assume that the volume dependent part is the same for all relevant concentrations and that $\eta_{\text{H(D)}}$ can be written as the sum of a concentration dependent and a volume dependent part: $\eta_{\text{H(D)}} = \eta_0(x) + \eta_1(V)$. From this we find that $\gamma_{\text{H(D)}}^{\eta} = -1/\eta_{\text{H(D)}} \partial \eta_1 / \partial \ln V$, where $\partial \eta_1 / \partial \ln V$ is concentration independent. So we have $\gamma_{\text{H(D)}}^{\eta} \propto 1/\eta_{\text{H(D)}}$ and, since $\lambda_{\text{H(D)}} \propto \eta_{\text{H(D)}}$, we have $\lambda_{\text{H(D)}} \gamma_{\text{H(D)}}^{\eta} \simeq \text{constant}$. As a consequence $\lambda_{\text{H(D)}} \gamma_{\text{H(D)}}^{\eta}$ and $\lambda_{\text{Pd}} \gamma_{\text{Pd}}^{\eta}$ in Eq. (8) will also cancel for substoichiometric $\text{PdH}_x(\text{D}_x)$.

Taking the previous into account we calculated $\partial \ln T_c / \partial P$ as a function of T_c for PdH_x and PdD_x . The results are shown in Fig. 6. They give the correct concentration dependence of $\partial \ln T_c / \partial P$.

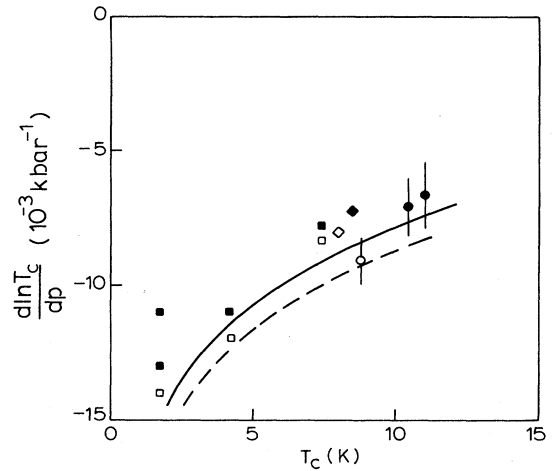


FIG. 6. Pressure dependence of substoichiometric palladium hydrides and deuterides. The horizontal axis gives the T_c which is a measure for the hydrogen (deuterium) concentration. The open (solid) symbols give the results for Pd-H(D). The squares (diamonds) are from Ref. 42 (43). The circles indicate present results. The dashed (solid) curve gives the theoretical result for Pd-H(D) with the parameters given in the text.

V. CONCLUSIONS

We have synthesized stoichiometric PdH and PdD in a diamond anvil cell and measured *in situ* the pressure dependence of the superconducting transition temperature. The volume dependence of the electronic parts of the electron-phonon coupling parameter was calculated. All other quantities entering the pressure dependence of the T_c could be obtained from literature. Without fitting parameters we reproduced the experimental pressure dependence of the T_c of PdH and PdD. We also could reproduce the pressure dependence for substoichiometric palladium hydrides. On the basis of the present results we conclude that the anharmonicity and the Debye-Waller factor give an adequate quantitative description of the isotope effects and the pressure dependence in the superconducting transition temperature of the Pd-H(D) system.

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