

anomalies in dilute Ti alloys are uncertain. With reference to the former alloys, Brailsford and Overhauser²³ have suggested that resistivity minima are due to temperature-dependent, elastic s - d exchange scattering, where the temperature dependence results from a progressive ferromagnetic ordering of nearest-neighbor pairs of paramagnetic ions as temperature is reduced. Bailyn²⁵ has suggested that a resistance minimum will occur if a ferromagnetic to antiferromagnetic transition of the localized moments takes place. Yosida⁵ has shown that cross terms in the expression for the elastic scattering potential, arising from the spin-dependent exchange interaction and the ordinary spin-independent Coulomb interaction between conduction electrons and localized moments, will give rise to a negative magnetoresistivity which is just proportional to the square of the magnetization, as has been observed experimentally in Cu-Mn⁷ and Cu-Co.⁸ The applicability of these ideas to the case of dilute Ti alloys might be tested by low-temperature susceptibility, specific heat, electron spin resonance, and neutron scattering experiments.

The relationship of the presently indicated magnetic interactions to the unusual alloying dependence of the superconducting transition temperature of Ti is also somewhat obscure. Investigations to see if the usual superconducting isotope effect exists⁵⁸ in pure Ti and specific heat measurements to determine the alloying dependence of the electronic density of states in dilute Ti alloys⁵⁹ would be of interest.

ACKNOWLEDGMENTS

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⁵⁸ The usual superconducting isotope effect appears to be absent in the case of the transition metal Ru: T. H. Geballe, B. T. Matthias, G. W. Hull, Jr., and E. Corenzwit, *Phys. Rev. Letters* **6**, 275 (1961).

⁵⁹ For such measurements on nondilute bcc Ti-Mo alloys and a discussion of the results with regard to the strong alloying dependence of the superconducting transition temperature in this system see R. R. Hake, *Phys. Rev.* **123**, 1986 (1961).

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Electrical Resistivity and Thermoelectric Power of Palladium after Hydrogen Desorption

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The electrical resistivity and thermoelectric power of desorbed palladium-hydrogen samples have been measured as functions of temperature from 4.2 to 300°K, and 77 to 273°K, respectively. The thermoelectric power of the desorbed specimens lies intermediate between the values of annealed and cold-worked palladium. An increase in the residual resistivity and a decrease in the value of $d\rho/dT$ is found for the desorbed samples. The results are explained in terms of an experimentally observed expanded lattice.

INTRODUCTION

IT is well known that palladium can absorb large amounts of hydrogen. In order to accommodate the hydrogen in interstitial octahedral sites,¹ the palladium lattice expands linearly by approximately 3%. For H/Pd atom ratios up to 0.03 the cube edge of the unit cell expands continuously from 3.88 to 3.89 Å (α phase). For ratios greater than 0.03 a lattice constant of 4.02 Å is observed (β phase). These two phases coexist up to a H/Pd atom ratio of 0.57; above this concentration, only the β phase is observable.² Some investigators² have reported complete recovery of the expanded

lattice after desorption and others³ have reported some residual expansion.

In an earlier investigation by the present authors,⁴ measurements were made of the effects of hydrogen absorption on the resistivity of annealed 99.995 at.% Pd, 90 at.% Pd-10 at.% Ni, and 83 at.% Pd-17 at.% Ni. After measurement, the hydrogen was removed from the specimens by heating them between 300 and 800°C for several minutes in vacuum. Two room temperature resistivity measurements were made, ρ_i (initial resistivity after annealing and prior to absorp-

³ G. Chaudron, A. Portevin, and L. Moreau, *Compt. rend.* **207**, 235 (1938).

⁴ A. I. Schindler, R. J. Smith, and E. W. Kammer, *Proceedings of the Tenth International Congress of Refrigeration, Copenhagen, 1959* (Pergamon Press, New York, 1960), Vol. 1, p. 74.

¹ J. E. Worsham, M. K. Wilkinson, and C. G. Shull, *J. Phys. Chem. Solids* **3**, 303 (1957).

² F. A. Lewis, *Metals Rev.* **4**, 132 (1960).

tion) and ρ_f (recovery resistivity after desorption). $\rho_f < \rho_i$ for all specimens. Also, a hysteresis effect in the lattice was observed; that is, the lattice did not return to its initial spacing. Since $\rho_i - \rho_f > \rho_0$ (ρ_0 = residual resistivity of the annealed Pd at 4.2°K) and $l_i \neq l_f$ (where l_i and l_f are the initial and final values of the lattice parameter), it was concluded that the temperature dependence of the resistivity would be modified for palladium after the desorption of hydrogen.

In order to clarify the effect of hydrogen absorption and desorption on the resistivity and lattice parameter of palladium, resistance measurements were made between 4.2 and approximately 300°K. In addition, since it has been shown⁵ that the thermoelectric power is extremely sensitive to imperfections, measurements of the thermoelectric power were also made on similar samples between 77 and 273°K. Finally, to check on the hysteresis effect in the lattice spacing, precision lattice parameter measurements were made on annealed palladium and palladium after hydrogen desorption.

EXPERIMENTAL PROCEDURE

For the resistivity measurements, four palladium wires of 99.995 at.% purity and 0.015-in. diam were used. Each wire was mounted circumferentially around a Bakelite tube. A copper-constantan thermocouple was tied and cemented to the middle of each wire. Current and potential leads were spot welded to each end of the wires. Resistance measurements were made between 4.2 and approximately 300°K for the wires in the following conditions: unannealed, annealed, charged with hydrogen (β -phase Pd), and after hydrogen desorption (referred to as Pd_{II}). The annealing step was omitted on the fourth wire. The palladium was annealed by pulsing each sample several times with a current sufficient to cause it to heat to about 800°C in vacuum. Sustained heating would have heated up the Bakelite cylinder even though the specimens were not in complete contact with the cylinder. The β -phase Pd was obtained by placing the cylinder with the annealed specimens in a 0.1 normal H₂SO₄ solution and cathodically charging the specimens with hydrogen using platinum as the anode. For both annealing and absorption of hydrogen, resistance values were taken to ensure the completeness of each procedure. Annealing was continued until no further decrease in resistance could be noted. The charging bath time was seldom more than 2 h at currents from 10 to 100 mA for the samples used. However, the absorption process at room temperature takes several days, since the hydrogen must diffuse into the specimen. During the diffusion period, the resistance of the specimens gradually increases and then levels off at some value approximately 80% higher than its original value at room temperature, indicating an H/Pd atom ratio of at least 0.6. In addition to the resistance measurements, x-ray diffraction

examinations were made and the α phase was not detected. The diffraction tests were done on independent strip samples that were subjected to the same conditions as the wires.

The Pd_{II} was obtained by heating the hydrogen-charged specimens in vacuum to at least 300°C. For the periods of heating used ($\frac{1}{2}$ h or less) the results are independent of the desorption temperature up to 800°C. Methods for determining the success of the desorption are: final room temperature resistance measurements (always lower than preabsorption value at room temperature), lattice parameter measurements (absence of β -phase Pd), and vacuum fusion techniques in which the total amount of residual hydrogen can be measured.

All resistance measurements were made with a K-3 potentiometer by measuring the potential drop across the sample and a standard resistor. The current was reversed for each measurement to eliminate extraneous voltages due to thermals in the current and potential contacts. The temperature variation was accomplished by natural boiloff of liquid helium and then liquid nitrogen between 4.2 and 300°K. At 4.2, 77°K, and room temperature, extraneous emf's were at a minimum because of long stabilization periods.

The thermoelectric power measurements for the specimens were made between 77 and 273°K relative to an annealed palladium wire standard. The thermoelectric power of the palladium standard was obtained by comparing it with the known thermoelectric power of high-purity annealed copper. For all measurements one junction was kept at 77°K and the other junction was varied from 77 to 273°K by changing the amount of immersion of the system. A copper-constantan thermocouple was used as the temperature sensing element, and the voltages were measured with a six-dial Rubicon potentiometer which can be read to 10⁻⁸ V. Three types of palladium samples were used, (a) as drawn (Pd_{un}), (b) annealed (Pd_a) and (c) after hydrogen desorption (Pd_{II}). After the desorption process, the hydrogen concentration was measured by the vacuum fusion

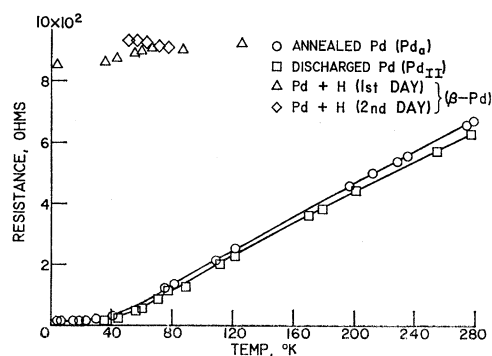


FIG. 1. Effect of temperature on resistance of Pd in following states: annealed, charged with hydrogen, and after desorption of hydrogen.

⁵ B. J. Van Ooyen, Appl. Sci. Research **5B**, 442 (1956).

method and was found to be less than 17 ppm by weight. The same method yielded values of 33 ppm of hydrogen by weight, before charging.

Finally, x-ray lattice parameter measurements were made at room temperature on samples of annealed palladium and palladium after hydrogen desorption.

RESULTS

Figure 1 shows the variation of resistance with temperature for annealed Pd, Pd_{II}, and β -phase Pd. Unannealed Pd is not shown, since it is very similar to annealed Pd. The plot for β -phase Pd is included primarily to show the effect of hydrogen absorption on the resistance of Pd. The two sets of data points for β -phase Pd are for different days of measurement and show that the diffusion of hydrogen into Pd is still taking place at approximately 77°K. Denoting the difference in resistance of the curves of annealed Pd and Pd_{II} by ΔR , it is easily seen that $|\Delta R|$ decreases with decreasing temperature. In Fig. 2, which is a magnified view of the lower section of Fig. 1, $|\Delta R|$ goes to zero and then increases for decreasing temperature. These graphs are representative of the three palladium specimens used in this experiment. There is a suggestion of a resistivity minimum for Pd_{II}.

As stated, the annealing step was omitted for wire 4. The resistivity results for wire 4 were somewhat similar to the results for the other three specimens, that is, $\rho_{un} > \rho_{II}$ above 20°K but $\rho_{un} < \rho_{II}$ at 4.2°K. (ρ_{un} and ρ_{II} are the resistivity values prior to charging and after discharging, respectively.)

Table I gives the resistance and resistivity values of specimens 1 to 4 at 4.2, 77, and approximately 300°K. At these temperatures thermal equilibrium of the systems was obtained and the measurements of potential and temperature were made under equilibrium conditions.

TABLE I. Electrical resistance of Pd-H systems. (Pd_{un}, unannealed Pd; Pd_a, annealed Pd; β -Pd, annealed Pd+H; Pd_{II}, (β -Pd-H); discharged at $\approx 700^\circ\text{C}$; resistance, $10^{-2} \Omega$.)

Specimen		Liquid He temperature	Liquid N ₂ temperature	Room temperature
1	Pd _{un}	0.1497	1.2065	6.9350 at 287.4°K
	Pd _a	0.1049	1.1692	6.8843 at 288.0°K
	β -Pd	8.5620	9.1425	12.4710 at 296.1°K
	Pd _{II}	0.1105	1.1190	6.7610 at 297.4°K
2	Pd _{un}	0.1476	1.2077	6.9311 at 288.5°K
	Pd _a	0.1068	1.1761	6.9106 at 288.5°K
	β -Pd	8.2690	8.9310	12.3860 at 296.1°K
	Pd _{II}	0.1125	1.1260	6.7750 at 297.8°K
3	Pd _{un}	0.1483	1.2213	7.2282 at 296.9°K
	Pd _a	0.0983		
	β -Pd	8.6910	9.3245	12.6750
	Pd _{II}	0.1035	1.1230	6.8185 at 296.5°K
4	Pd _{un} ^a	0.2068	1.8455	10.9012 at 297.0°K
	Pd _{II} ^a	0.2082	1.7259	10.6320 at 303.0°K

^a $10^{-6} (\Omega) (\text{cm})$.

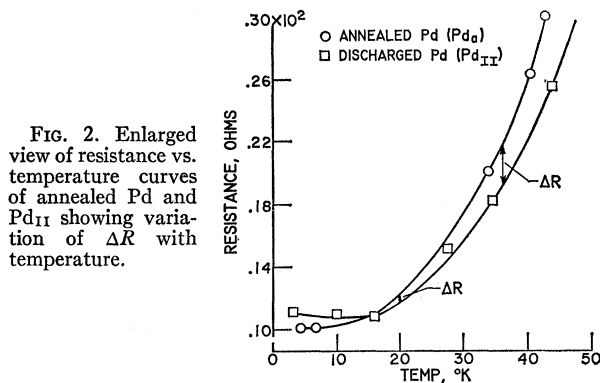


FIG. 2. Enlarged view of resistance vs. temperature curves of annealed Pd and Pd_{II} showing variation of ΔR with temperature.

The thermoelectric power vs temperature results are summarized in Fig. 3. The upper curve shows the plot for the heavily cold-worked wire (Pd_{un}), while the lowest curve shows the effect of a 900°C, 2-h anneal. Between these curves is a plot of the thermoelectric power of the specimen Pd_{II} (after the sequence of hydrogenation, followed by a 300°C vacuum anneal to remove the hydrogen). An obvious shift from the annealed toward the cold-worked values is apparent.

Back reflection, the Debye-Scherrer method, and graphical analysis of x-ray patterns have shown that a slight increase in lattice parameter occurs in palladium as a result of the absorption and desorption of hydrogen. The increase is approximately 1 part in 4000, in agreement with earlier measurements.

In order to obtain more information about the nature of the expanded lattice, a calculation of θ_R (characteristic temperature in quantum theory of electrical resistance and comparable to the Debye temperature θ_D) was made using one of the methods of Kelly and MacDonald.⁶ The equation is

$$(T/R)dR/dT = 1 + (X/G)dG/dx, \quad (1)$$

where G is the Grüneisen function and $X = \theta/T$. Kelly and MacDonald have plotted $1 + (X/G)dG/dx$ as a function of X . In this method the dependence of θ_R on the electron-lattice interaction constant may be neglected. The results are shown in Figs. 4 and 5. The θ_R values as calculated from the resistivity data are low, since there were no corrections made for the

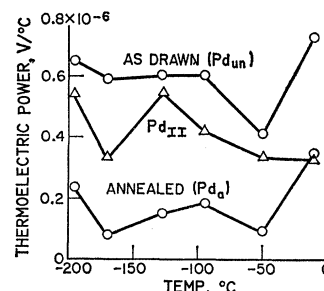


FIG. 3. Shift of thermoelectric power of Pd_{II} (after absorption and desorption of hydrogen) from annealed toward unannealed value.

⁶ J. M. Kelly and D. K. C. MacDonald, Can. J. Phys. **31**, 147 (1953).

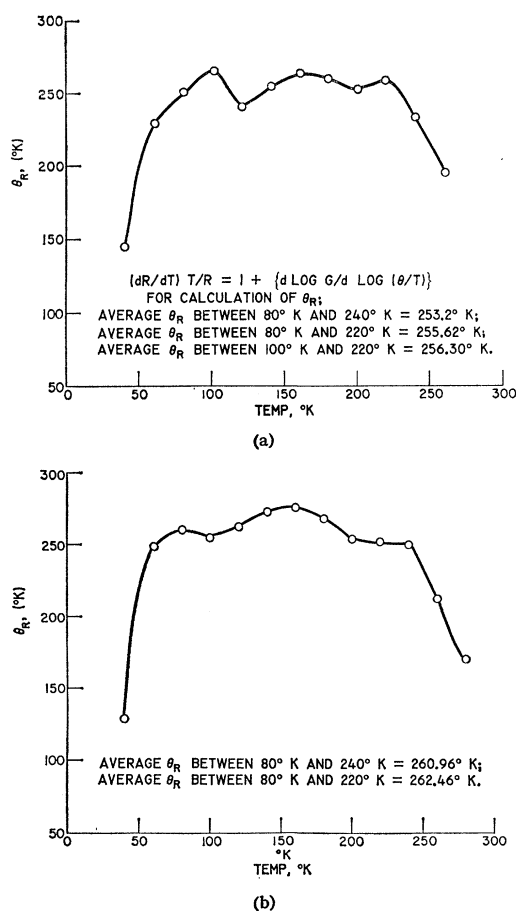


FIG. 4. (a) Annealed state. (b) Desorbed state. Characteristic temperature θ_R for specimen 1.

residual resistivities. If these corrections are applied to the annealed palladium specimens, it is found that the θ values agree quite well with those calculated from specific heat ($\theta = 275^\circ\text{K}$) and other resistivity data ($\theta = 270^\circ\text{K}$).⁷ As usual, the θ values are averaged over that portion of the curve where the variations in θ are small for large variations in T , that is, over the flattest portion of the curve. It is easily seen that the θ values of Pd_{II} are greater by approximately 10°K than those of the original palladium specimens.

DISCUSSION

The electrical resistivity of a metal can be written as

$$\rho = \rho_0 + \rho_T,$$

where ρ_0 is the residual resistivity and ρ_T is the phonon contribution to the resistivity. The shift in the thermoelectric power of the desorbed palladium toward the unannealed palladium would suggest that the process of absorption and desorption of hydrogen results in a

lattice with residual imperfections. These imperfections in the lattice would of course increase ρ_0 , and this is observed, since Pd_{II} has a higher resistivity than annealed Pd (Pd_a) at 4.2°K. However, if the only difference in Pd_a and Pd_{II} were the imperfections, then $\rho_T(\text{Pd}_a) = \rho_T(\text{Pd}_{II})$. This, however, is not the case. The increase in ρ_0 for Pd_{II} is more than compensated for by the decrease in ρ_T , and at room temperature Pd_{II} has a lower resistivity than Pd_a.

Phenomenologically the decrease in the phonon contribution to the resistivity can be described in terms of the modified lattice dynamics of the palladium after hydrogen desorption (Pd_{II}). The expanded lattice yields an approximate 10° increase in the value of θ . This increase in θ is usually associated with a stiffer lattice. (It may be noted that the Brinell hardness was also observed to increase by a factor of 2.) In the case of a simple metal, one can describe the resistivity in terms of θ .

$$\rho_T = T/m\theta^2, \quad (2)$$

or

$$\Delta(\partial\rho_T/\partial T) = -(2/m\theta^3)\Delta\theta, \quad (3)$$

where m is atomic mass. The observed increase in the θ results in a decrease in $\partial\rho_T/\partial T$ as has been experimentally observed.

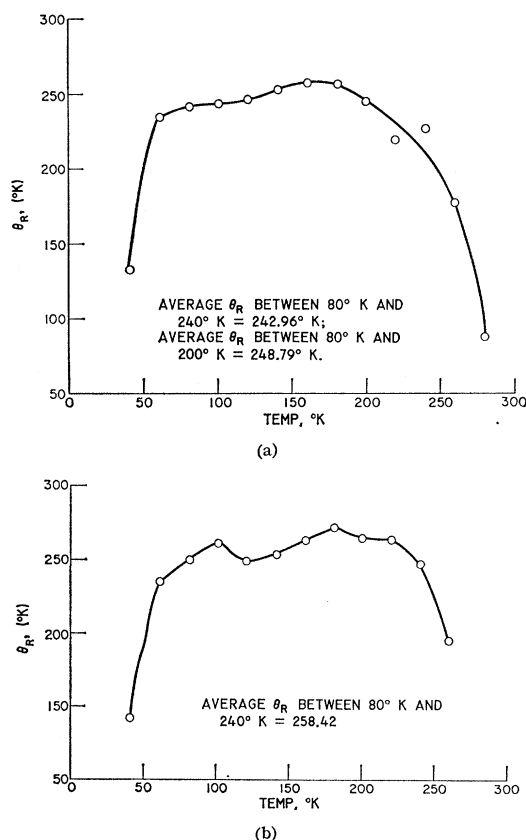


FIG. 5. (a) Annealed state. (b) Desorbed state. Characteristic temperature θ_R of specimen 2.

⁷ M. F. Mott and H. Jones, *Theory of the Properties of Metals and Alloys* (Oxford University Press, New York, 1936), p. 14.

However, it would be expected that expanding the lattice of a normal metal should result in a "looser" lattice and θ ought to decrease. In the case of palladium, which is a transition metal, it is evident that something quite different is occurring. The residual resistivity of a transition metal is generally written as the sum of contributions arising from s - s scattering and from s - d scattering:

$$\rho_0 = \rho_{ss} + \rho_{sd}. \quad (4)$$

For palladium, the ratio of s - s to s - d scattering is approximately 1 to 5, and this is presumed to result from the large density of d states N_d evaluated at the Fermi energy. However, in the neighborhood of the Fermi energy, N_d falls rapidly with energy, and any modification of the filling of this band will have a large effect on the resistivity. Since the Fermi energy is a function of temperature, the rapid decrease in N_d with energy has a decided effect on the temperature dependence of the resistivity. One can show that the temperature dependence of the resistivity can be written⁸

$$\rho(\zeta, T) = A(T)(1 + 2\alpha\gamma T) \times \left\{ 1 - \frac{\pi^2}{6}(KT)^2 \left[3 \left(\frac{1}{N_d} \frac{dN_d}{dE} \right)^2 - \frac{1}{N_d} \frac{d^2 N_d}{dE^2} \right]_{\zeta_0} \right\}, \quad (5)$$

where ζ is the Fermi energy; ζ_0 is the Fermi energy at $T=0$, α is the coefficient of expansion, and γ is the Grüneisen constant. If a normal inverted band shape is assumed for the d band, Eq. (5) can be reduced to the following:

$$\rho(\zeta, T) = A(T)(1 + 2\alpha\gamma T) \left[1 - \frac{\pi^2}{6} \left(\frac{kT}{E_1 - \zeta_0} \right)^2 \right], \quad (6)$$

where $E_1 - \zeta_0$ is the energy width of the unfilled portion of the d band.

The $A(T)$ part of Eq. (6) arises from the normal phonon scattering and is proportional to $N_d(E)$ through the transition probability $P(\vec{k}_m, \vec{k}_n)$, where \vec{k}_m is the electron state before scattering and \vec{k}_n its state after scattering. The second part $(1 + 2\alpha\gamma T)$ arises from the expansion of the lattice due to temperature; the remainder of the term is a consequence of the temperature dependence of s - d scattering. For a metal like palladium, this latter part of the expression is dominant, and as a result the temperature dependence of the electrical resistivity is concave toward the temperature axis. This departure from linearity will be inversely proportional to the square of the width in energy of the unfilled portion of the d band. Since

⁸ H. Jones, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 19, p. 267.

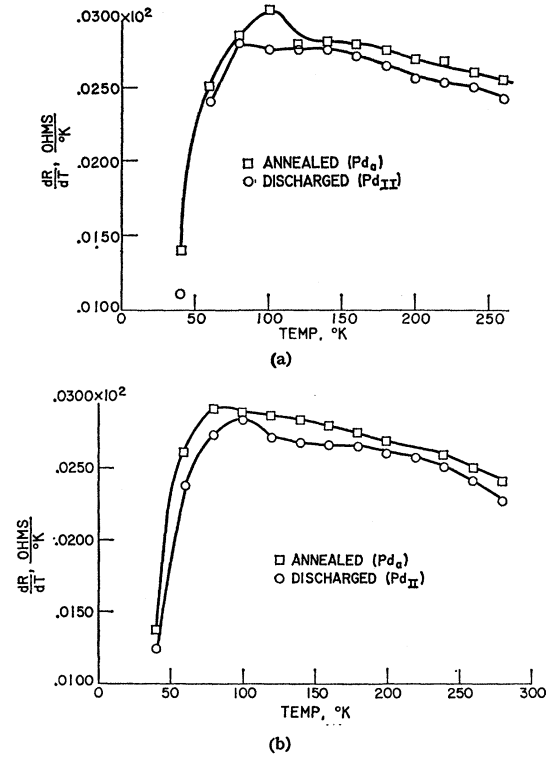


FIG. 6. Variation of the slope, dR/dT , with temperature for Pd in annealed state and after desorption of hydrogen. (a) Specimen 1. (b) Specimen 2.

this departure is greatest for Pd_{II} , it would appear that the expanded palladium lattice causes a redistribution of the s and d electrons so that the number of holes in the d band is decreased. This decrease in $N_d(E)$ also diminishes the normal phonon contribution from $A(T)$ to ρ in Eq. (6). It is interesting to note that $\partial\rho(\text{Pd}_{\text{II}})/\partial T < \partial\rho(\text{Pd}_a)/\partial T$ at all temperatures, as shown in Fig. 6, and $\partial\rho(\text{Pd}_{\text{II}})^{T+30}/\partial T \cong \partial\rho(\text{Pd}_a)^{T+30}/\partial T$ in the temperature region where the last term in Eq. (6) is dominant. Since an expansion of the lattice of 1 part in 4000 at room temperature is equivalent to a thermal expansion with $\Delta T \cong 30^\circ$, it appears that the distribution of s and d electrons depends on temperature and change in lattice constant.

If this model is correct, several other physical properties would be affected. Magnetic susceptibility, Hall effect, and electronic specific heat measurements all depend on occupation of the s and d bands. Preliminary susceptibility measurements on desorbed palladium-hydrogen specimens show no significant changes, but it is possible that the magnetic susceptibility is not a sensitive enough parameter. Measurements on the other two properties are being planned.