

Introduction

For some time it has been known that the magnetic susceptibility of Pd decreases as hydrogen is absorbed and reaches zero at approx. Pd H_{0.6} to Pd H_{0.7} (8).

(8) H.P. Smith "Hydrogen in Metals" University of Chicago Press, Chicago, Illinois (1949)

It has also been known for many years that at Pd H_{0.6} the Pd metal expands as a phase transition that is only slightly greater in lattice parameter, and this phase exists

PART II

Magnetic Susceptibility Effects on

4.08 Removal of Hydrogen from Phase

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was the most satisfactory at explaining the effect. Accord-

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However Michel and Gallucci (9) observed all of the

(9) J. Michel and E. Gallucci, Compt. Rend. 208 454 (1959)

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10 The author wishes to extend his deep appreciation to Professor

14 T.R.P. Gibb Jr., without whose patient guidance this paper

18 would not have been possible.

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Introduction

For decades it has been known that the magnetic susceptibility of Pd decreases as hydrogen is absorbed and reaches zero at approx. Pd H_{.6} to Pd H_{.7} (8).

(8) D.P. Smith "Hydrogen in Metals" University of Chicago Press, Chicago, Illinois (1948)

It has also been known for many years that at Pd H_{≤.03}. The Pd metal expands as a phase termed α that is only slightly greater in lattice parameter, and this phase coexists with a second β phase of parameter approximately 4.02 Å up to stoichiometry \sim Pd H_{.6} whereupon the β phase appears solely. (8) Thus it was necessary to explain why the β phase was diamagnetic and the familiar band theory (5) was the most satisfactory at explaining the effect. According to this explanation the portion of the density of states curve for Pd to the right of the Fermi level shows that Pd lacks approximately .55 electron in its d band. When H₂ is absorbed the electron from the hydrogen is donated to the d band therefore at hydride composition of approximately Pd H_{.55} there should be no unpaired electron spin in the d band and the substance should be diamagnetic.

However Michel and Gallissot (9) removed all of the

(9) A. Michel and M. Gallissot: Compt. Rend. 208 434 (1939)

hydrogen from β phase palladium hydride with a high voltage device at room temperature and observed no increase in susceptibility. Thus they postulated that volume effects in the lattice, not filling of a hold in the d band was responsible for the decrease in magnetic susceptibility.

T.R.P. Gibb Jr. (10) noted that if one extrapolates the

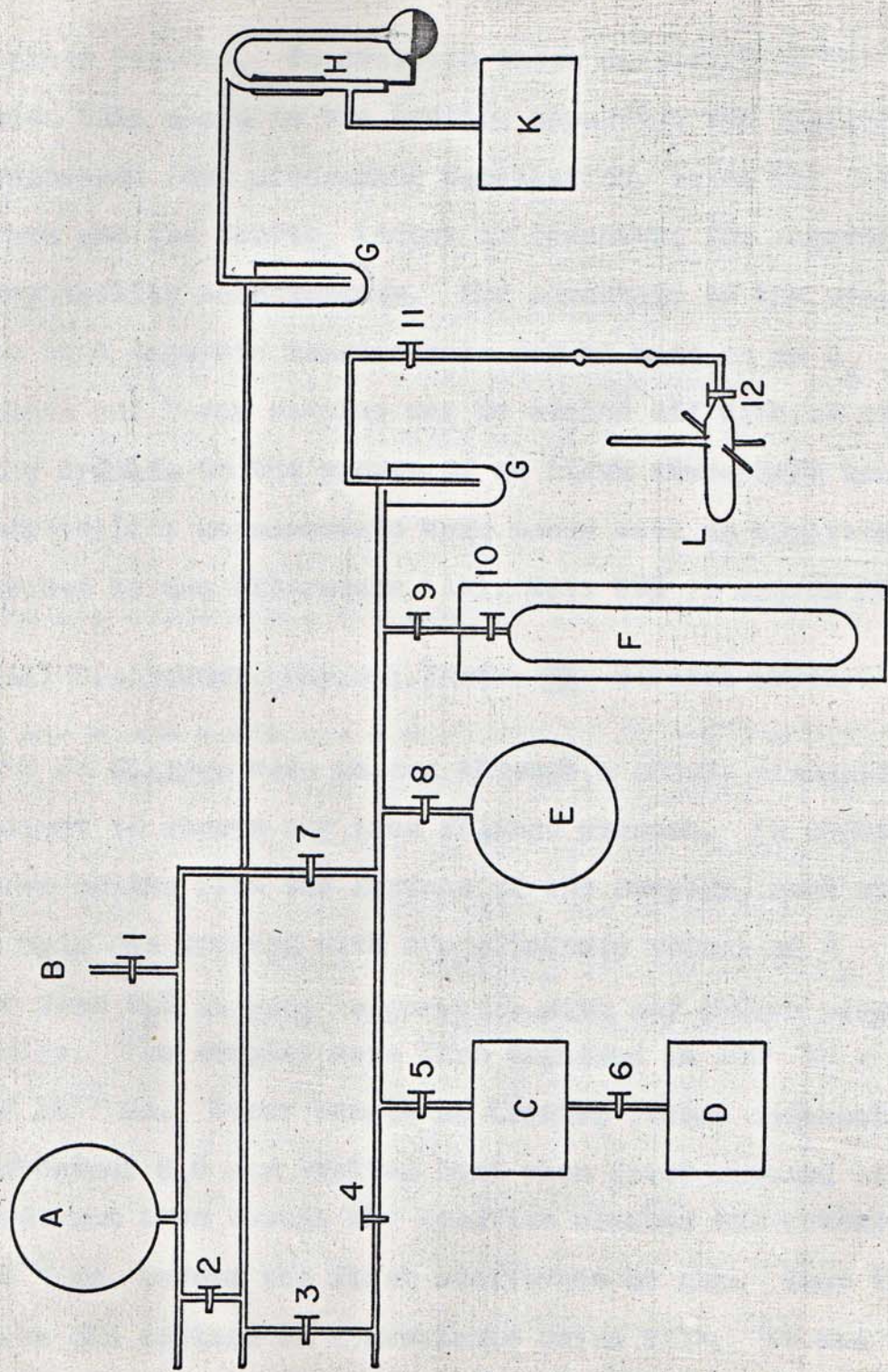
T.R.P. Gibb Jr. "Lattice-Distension and the Magnetic Susceptibility of Palladium Hydride"- Tufts Univ. 1968, to be published

curve of paramagnetic susceptibility vs. relative volume of the unit cell the value at which pure palladium becomes diamagnetic is surprisingly close to the relative volume of the β phase lattice. T.R.P. Gibb and W.A. Norder attempted to confirm the results of Michel and Gallissot and their results were partially confirmed. Accordingly in this investigation Dr. R.J. Roy and myself wished to prepare pure β phase hydride and pump off hydrogen to some stoichiometry below $PdH_{0.6}$ without forming any α phase and wished to observe if the magnetic susceptibility remained constant. A zero paramagnetic susceptibility at hydrogen contents lower than that of $Pd_{0.6}$ would refute the band theory explanation of this effect, and reinforce Michel and Gallissot and T. R. P. Gibb's speculations. If it were impossible

to prevent formation of β phase we at least desired to obtain a graph of magnetic susceptibility vs. stoichiometry on desorption that would show a lower susceptibility than the corresponding stoichiometry on absorption. Such would infer that the desorption stoichiometry had a greater percentage of diamagnetic β phase than the corresponding absorption stoichiometry.

Experimental

The hydrides were synthesized with the hydride synthesis line illustrated and described in the Figure 2. Tank hydrogen was passed through a catalytic Deoxo purifier and drierite before entering the system. The vacuum system could be evacuated to 10^{-5} mm. In the attempted earlier synthesis a U H₃ getter was used to generate the H₂ but it became very sluggish to charge and was finally abandoned. The early attempted syntheses employed an approximately 200 ml reaction tube and a metal boat for holding the palladium. When the synthesized hydrides were transferred in the inert atmosphere box to an analysis tube, the lock had to be evacuated with the hydride exposed. This procedure was found to remove nearly all of the hydrogen from the sample due to the hydrides appreciable equilibrium pressure in a vacuum at r. t. Subsequent analysis of these samples showed no H₂ evolved and X-ray powder patterns showed only



phase present. To overcome these difficulties the reaction tube shown in the hydride apparatus was designed. It contained four protruding capillaries, three for X-ray analyses and the fourth, larger in diameter, for magnetic susceptibility measurements. The advantage of the apparatus is that magnetic measurements may be made in an H_2 atmosphere and X-ray samples may be sealed off without exposing the hydride to the vacuum of an inert atmosphere box. Susceptibility measurements were taken with an apparatus described in the literature (11). Metz 99% .8 micron Pd used.

(11) W.A. Norder, Rev. Sci. Instr. 31 848-851 (1960).

The Pd filings were passed through a screen alongside a magnet to remove any iron filings present. In order to remove oxides from the surface of the samples, each weighed sample was treated with a preliminary volume of H_2 at r.t. to form H_2O at room temperature with any oxygen present as oxide. The samples were then degassed at 100° to a pressure of 10^{-5} mm. Every sample so treated formed noticeable amounts of H_2O and evolved heat when first exposed to dried hydrogen even though the reaction chamber was evacuated to 10^{-5} mm. before the first admittance of gas. Thus the palladium did contain an appreciable oxide film. It was found through trial and error with preliminary samples that Pd

absorbs negligible amounts of H_2 at r.t. but that absorption is appreciable at 60° to $80^\circ C$. Thus each weighed and previously deoxidized Pd sample was exposed to H_2 in the reaction tube from a calibrated volume of the vacuum line. The temperature was raised to $100^\circ C$, and the reaction tube allowed to cool at about 10° an hour to r.t. The stoichiometries were calculated from observing pressure changes as is described in a following section. Using this procedure it was possible to prepare hydrides of stoichiometries very close to the limiting ratio of Pd $H_{.7}$ at r.t.

An interesting observation is that on heating, appreciable sintering occurs when Pd metal is heated above $200^\circ C$, and that some sintering occurs even at 80° to $100^\circ C$, during hydriding of the Pd samples. Such behavior is quite surprising considering the high (over $1500^\circ C$) melting point of Pd. Due to this behavior the hydrides in the special reaction tube were in the form of a porous cake after the reactions. Since the mass couldn't be broken up manually without exposure to air, it was vibrated within the tube. A loudspeaker was used as the vibrator. It was modified by cementing a plastic hollow cylinder to the moving portion so that the plastic cylinder agitated the tube. An audio oscillator and amplifier provided vibration of the proper frequency so that the porous mass within the tube was reduced to powder after about two days of vibration. Such procedure was necessary in order for the hydride to be transferable into the four capillaries of the

reaction tube.

Another interesting observation is the intensity of the exothermic reaction when the hydrides are exposed to air. Water is immediately formed and so much heat is evolved that small particles glow in the reaction tube. The reaction could be due either to oxygen reacting directly with the hydride, or to metallic Pd catalyzing the reaction between O_2 and H_2 evolved from the surface of the hydride.

(14) Mayer, B. M.S. Thesis, Tufts University, 1937.

$$V_1 = \frac{P_2 V_2}{P_1} - (V_2 - h_1)$$

V_1 = unknown volume

P_2 = Pressure in calibrated flask before expansion

P_1 = Pressure in calibrated flask + unknown volume after expansion

V_2 = Volume of calibrated flask

h_1 = correction for volume taken up by the Hg.

$$h_1 = W \cdot F^2 (h - 50) = .2837 (h - 50)$$

h being height in cm of the Hg.

Calibrated volumes

Volume = 4 + 5 + 7 + 8 + 13 (see Figure 2)

= 37 ml

Volume of reaction tube L = 49.4 ml.

CALIBRATION OF THE SYSTEM

The volume of two sections of the vacuum system was obtained by expanding a known pressure and calibrated volume, known calibrated bulb $v \approx 988.9$ ml.

The following formula was used: (12)

 (12) Hayes, H. M.S.Thesis, Tufts University, 1957

$$V_1 = \frac{P_o V_o}{P_1} - (V_o - h_1)$$

V_1 = unknown volume

P_o = Pressure in calibrated flask before expansion

P_1 = Pressure in calibrated flask + unknown volume after expansion

V_o = Volume of calibrated flask

h_1 = correction for volume taken up by the Hg.

$h_1 = \pi r^2 (h-50) = .2927 (h-50)$
 h being height in cm of the Hg.

Calibrated volumes

Volume 4 + 5 + 7 + 8 + 12 (see Figure 2)

= 923.7 ml

Volume of reaction tube L = 49.4 ml.

CALCULATION OF HYDRIDE STOICHIOMETRY

The stoichiometry of the hydride may be computed during the synthesis by observing the decrease in pressure as the known volume of hydrogen is admitted to the reaction chamber. All pressure readings must of course be made at the same temperature (room temperature in these runs).

$$P_1 V_1 = (V_2 + V_3 + V_4) P_2$$

P_1 and V_1 = pressure and volume in calibrated system.

P_2 = pressure in system + reaction tube after reaction

$V_2 + V_3 + V_4$ = total effective volume after reaction

V_2 = known volume reaction tube

V_3 = volume H_2 absorbed by Pd at P_2 pressure and 298° K temperature.

$$\therefore \frac{P_2 V_3}{298} = \frac{76 \times V_4}{273}$$

V_4 = Volume absorbed at S.T.P.

$$E_1 = \frac{V_4 \text{ ml}}{1.1207 \times 10^4 \text{ ml/equiv.}} = \text{equivalents } H_2 \text{ absorbed}$$

$$E_2 = \frac{\text{wt Pd}}{106.7} = \text{equivalents Pd}$$

$$\text{Stoichiometry} = Pd H_{\frac{E_1}{E_2}}$$

In the sample that was finally studied 2.3528 g of Pd absorbed 171.9 ml of H_2 at S.T.P. corresponding to a stoichiometry of Pd $H_{1.45}$. The sample was subjected to vibration to break down the porous mass. Susceptibility measurements

RESULTS

In order to take the hydrogen out of the sample under mild enough conditions to allow some survival of the β phase on desorption, the sample was exposed repeatedly to a calibrated line under vacuum next to the magnetic susceptibility apparatus (V of line = 1718 ml). By reading with a manometer the pressure on the line when the evacuated system is exposed to the reaction tube, we can calculate the volume released by the sample and from this the stoichiometry of the hydride in the reaction tube. After the number of expansions came to a total of at least 1 cm pressure the hydrides were placed in the magnetic susceptibility side-arm of the reaction tube and the susceptibility measured.

Due to experimental difficulties, accidents, and a time limit on this thesis there was time for only one run with a diamagnetic hydride sample. One early sample showed appreciable paramagnetism (1.714×10^{-6} e.g.s/g) although the stoichiometry came to Pd H_{0.68} and therefore it was discarded. The stopcock popped on another promising sample thus greatly delaying compilation of data.

In the sample that was finally studied 2.3528 g of Pd absorbed 171.9 ml of H₂ at S.T.P. corresponding to a stoichiometry of Pd H_{0.696}. The sample was subjected to vibration to break down the porous mass. Susceptibility measurements

showed the substance to be diamagnetic as is predicted in all the literature on magnetic effects of the PdH_2 system(5). The results of the data are shown in the forthcoming table. Correction is made in the first reading for the pressure of H_2 initially over the Pd H.696 (28.5 ml at S.T.P.) The pressures obtained upon expansion into the calibrated system were quite high at first but after 30 expansions the pressure of the H_2 became negligible. The total calculated volume given off by the sample (203ml) agreed quite well with the known total volume of H_2 at S.T.P. (200.4ml), considering the limited accuracy of reading the manometer.

CONCLUSIONS

The most striking part of the data is the result that the hydride remains diamagnetic at least until stoichiometry Pd H.₃. This effect strongly indicates that under the mild conditions of evacuation employed here the diamagnetic phase is slow to break down to paramagnetic and therefore at stoichiometries at least to Pd H.₃ the diamagnetic phase exists solely. Unfortunately since this run was originally meant to be a trial and I did not know what behavior would be observed, X-ray pictures were not taken during the run to confirm this. It is hard to explain diamagnetism for stoichiometries <.6 in any other way though since the phase, which is only slightly distended Pd metal, is

MAGNETIC SUSCEPTIBILITY VS. STOICHIOMETRY FOR DEGASSING PdH_{0.696}
INTO A CALIBRATED SYSTEM. V of H₂ over PdH_{0.696} initially=28.5 ml at S.T.P.

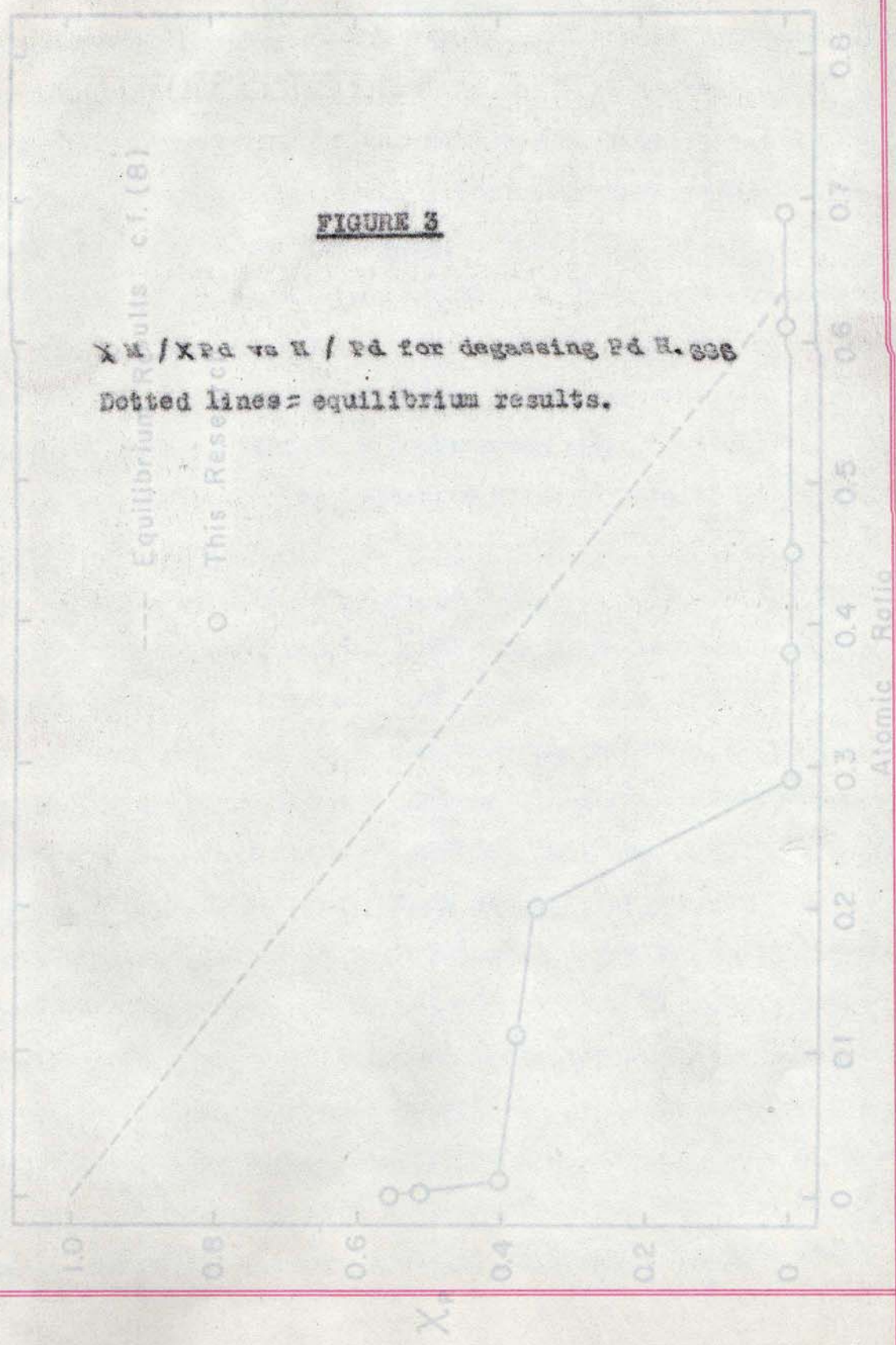
| Time between evac. | Evacua- tion | P (cm) | Vol. H ₂ S.T.P. | Equivalents H ₂ removed | Total Equivalents Removed | H/Pd | X Mx10 ⁻⁵ | X M Pd |
|--------------------|-----------------|-----------|-------------------------------|---------------------------------------|---------------------------------|------|-------------------------|--------------|
| | 1 | 2.02 | 11.84 | 1.19x10 ⁻³ | 1.19x10 ⁻³ | .61 | 0 | 0 |
| 30 min. | 2 | 2.30 | 17.84 | 4.25x10 ⁻³ | 5.44x10 ⁻³ | .45 | 0 | 0 |
| 30 min. | 3 | .80 | 16.57 | 1.48x10 ⁻³ | 6.92x10 ⁻³ | .38 | 0 | 0 |
| Overnight | 4a | .37 | | | | | | |
| 10 min. | 4b | .37 | | | | | | |
| 10 min. | 4c | .36 | | | | | | |
| 20 min. | 4 total | 1.10 | 22.79 | 2.01x10 ⁻³ | 8.96x10 ⁻³ | .29 | 0 | 0 |
| Overnight | 5a | .36 | | | | | | |
| 10 min. | 5b | .36 | | | | | | |
| 10 min. | 5c | .36 | | | | | | |
| 20 min. | 5 total | 1.08 | 22.34 | 1.99x10 ⁻³ | 1.095x10 ⁻² | .2 | 190.5 | .354 |
| Overnight | 6a | .35 | | | | | | |
| 10 min. | 6b | .35 | | | | | | |
| 10 min. | 6c | .35 | | | | | | |
| 20 min. | 6 total | 1.05 | 21.74 | 1.94x10 ⁻³ | 1.289x10 ⁻² | .11 | 204.8 | .381 |
| 30 min. | 7a | .16 | | | | | | |
| 10 min. | 7b | .16 | | | | | | |
| 10 min. | 7c | .30 | | | | | | |
| 10 min. | 7d | .21 | | | | | | |
| 10 min. | 7e | .21 | | | | | | |
| 10 min. | 7f | .20 | | | | | | |
| 80 min. | 7 total | 1.20 | 25.89 | 2.31x10 ⁻³ | 1.520x10 ⁻² | .01 | 217.2 | .404 |
| Overnight | 8a | .17 | | | | | | |
| 10 min. | 8b | .10 | | | | | | |
| 10 min. | 8c | .13 | | | | | | |
| 10 min. | 8d | .04 | | | | | | |
| 10 min. | 8e | .01 | | | | | | |
| 40 min. | 8 total | .45 | 10.8 | 8x10 ⁻⁴ | 1.61x10 ⁻² | .001 | 277.2 | .515 |
| Overnight | 9a | .000 | 0 | 0 | 0 | .000 | 321.2 | .558 |

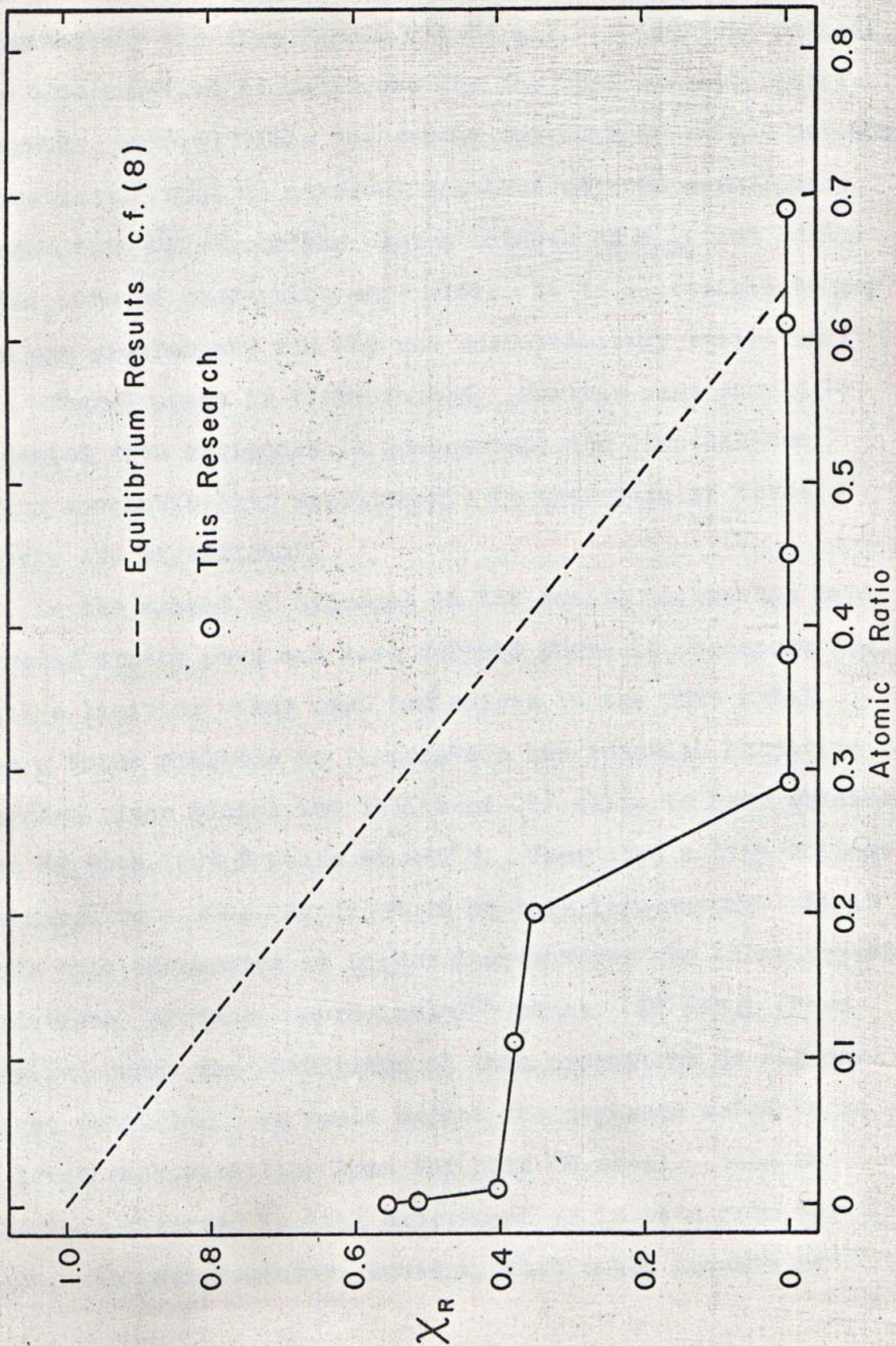
unquestionably paramagnetic. Pumping off substantial quantities of H_2 without changing the susceptibility confirms the work of Michel and Gallissot (9). This observation also tends to support lattice distension of Pd as proposed by Gibb (10) as the reason for the drop in susceptibility as H_2 is absorbed. It is not consistent with the proposal that filling of the approximately .6 hole in the d band causes the drop in paramagnetism, because were this the case pumping hydrogen off from stoichiometry .6 on down would remove spin pairing hydrogen electrons from the band causing an appreciable paramagnetic moment in the range (.6 to .3) where the hydride was found to be diamagnetic.

The accompanying graph illustrates these observations pictorially. The large increase in magnetic susceptibility on desorption from $Pd H_{.29}$ to $Pd H_{.2}$ indicates that in this range considerable defect β phase has broken down to α phase. ~~$2\alpha + \beta$~~ two-phase system probably exists between $PdH_{.29}$ and $Pd H_{.01}$. The relatively slight increases in magnetic susceptibility in this region indicate that comparatively small amounts of β phase are breaking down to α phase. It is not known whether the relatively great increase in susceptibility followed by smaller increases is a result of the experimental conditions or due to a fundamental phase change in the lattice in this stoichiometric region. All samples were treated under the same temperature (room) and

FIGURE 3

X_H / X_{Pd} vs H / Pd for degassing Pd H. 836
Dotted lines = equilibrium results.





approximately the same vacuum ($\approx .05$ mm). Since long periods were often required to calibrate the magnetic susceptibility apparatus, several times the sample was left overnight between evacuations. Such an interval may have allowed more β phase to decompose ~~to α~~ in the region between Pd H._{.29} and Pd H._{.2} if the rate of conversion were slow. It is impossible to say from one preliminary run why the susceptibility varies as it does after α phase is first formed. Further runs should be conducted with variances in temperature and time between taking susceptibility measurements to ascertain if these factors are significant.

As the amount of hydrogen in the sample approaches zero we would expect more and more defect β phase to decompose to α until a limiting value of α to β exists in the pure metal. Such a value probably is temperature and reaction condition dependent since Michel and Gallissot (9) claim to have obtained pure Pd with 100% β phase at -40°C . They used a high voltage discharge to remove the hydrogen at this temperature. It is known that desorption at higher temperatures and other drastic conditions produces appreciable α phase. If any β phase survived under the conditions of this experiment in the degassed palladium we would expect the degassed metal to be of lower susceptibility than the pure Pd metal. Such an effect is observed in this experiment as is seen from the graph. We must remember, however, that small amounts of

unevacuated H_2 remaining in the Pd face also could lower the susceptibility somewhat. X-ray analysis of the degassed sample showed strong α phase lines and three very faint lines in the front reflection region that at first were thought to be β phase. Accurate calculations however gave $a_0 \approx 4.3 \text{ \AA}$ not ≈ 4.02 therefore the nature of this phase is unknown.

Since no β phase was detected and since the unknown impurity is evidently present in very small quantity the low susceptibility can probably be attributed to residual hydrogen. This conclusion is by no means certain however. The low hydrogen stoichiometry region of the graph is somewhat inaccurate due to the low hydrogen pressures and the difficulty of reading them accurately. This inaccuracy in no way detracts, however, from the more accurately determined stoichiometries from Pd $H_{.69}$ to Pd $H_{.1}$. The results in this region support the dependence of magnetic susceptibility on the Pd-Pd distance, and casts doubt on the Mett and Jones explanation for the magnetic behavior (5). Since only one run was made, one must regard these results as tentative. More runs should be undertaken to ascertain at what stoichiometry the susceptibility increases from zero as hydrogen is removed from Pd $H_{.6}$. The effect of varying temperature and time between desorptions, and what effect very small amounts of hydrogen have on the susceptibility of palladium metal, also should be investigated.

The Magnetic Susceptibility of
Palladium Hydride

Respectfully submitted,

John H. Macmillan

Accepted by:

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Richard W. Hill

CHAIRMAN,
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The linear decrease of the paramagnetic susceptibility of palladium as it absorbs hydrogen is well known.¹ The portion of the diagram to the right of the Fermi level is usually drawn to indicate that palladium binds about 0.75 electron to fill the level. It has been suggested² that hydrogen donates a electron to fill this d level so that when the spins are paired, the substance should become diamagnetic. This latter is observed experimentally³ and is in contrast to the previously reported behavior of PdH_{0.75} rather than PdH_{0.5}. If the above explanation is correct, it would be possible to obtain a linear increase in susceptibility as hydrogen is removed from PdH_{0.75} which was attempted⁴ by a high-voltage method for extracting hydrogen without heating the sample and was obtained that all the hydrogen could be removed without any change in the magnetic susceptibility. These results were not confirmed by Lewis, et al.,⁵ using an electrolytic method for removing hydrogen. It was partially confirmed in this laboratory⁶ using a high-voltage method.

In the present series of experiments diamagnetic and slightly paramagnetic samples of palladium hydride were prepared from very fine (0.50- μ) palladium metal powder by alternately heating and cooling the metal in pure hydrogen (obtained by evolution from H₂O₂) in a temperature which never exceeded 200° above and below the room temperature. These samples evolved hydrogen at room temperature when the hydrogen pressure above them was below 10 atm. The magnetic susceptibility of samples of palladium hydride was continuously compressed to that of a standard (Mohl's H₂) while small volumes of quantities of hydrogen were removed from the sample in a separator which has been described previously.⁷ The results are shown in Figure 1. Curves 1 and 2 show that it is possible to remove a large fraction of the hydrogen from diamagnetic palladium hydride and that palladium hydride which is diamagnetic changes to an initial lower

Figure 1. The effect of desorption and absorption of hydrogen on the paramagnetic susceptibility of palladium.

hydrogen content, without changing the susceptibility (1,2). Curves 3 and 4 for the absorption of hydrogen by palladium are taken from Smith.¹ It thus appears that the band theory explanation is not valid for the desorption of hydrogen from palladium hydride and it may be that lattice expansion plays a more important role than was formerly thought. Further experimental and theoretical work is in progress.

Acknowledgment.—The authors are indebted to the U. S. Atomic Energy Commission for financial support for this work.

- (1) D. F. Smith, "Hydrogen in Metals," University of Chicago Press, Chicago, 20, 1947.
- (2) N. F. Mott, *Advan. Phys.* **14**, 335 (1966).
- (3) A. Michel and M. Gollison, *Canad. Jour. Chem.* **38**, 194 (1960).
- (4) J. C. Patton, F. A. Lewis, and I. Woodward, *Trans. Faraday Soc.* **59**, 1201 (1963).
- (5) T. E. P. Gibb, Jr., to be submitted.
- (6) W. A. Nordsieck, *Acc. Sci. (Ser.)* **31**, 235 (1960).

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Received March 15, 1968

The Magnetic Susceptibility of Palladium Hydride

Sir: The linear decrease of the paramagnetic susceptibility of palladium as it absorbs hydrogen is well known.¹ The portion of the density of states curve to the right of the Fermi level is usually drawn to indicate that palladium lacks about 0.55 electron to fill the d level. It has been suggested² that hydrogen donates its electron to fill this d level so that when the spins are paired, the substance should become diamagnetic. This latter is observed experimentally but at a composition variously reported but close to PdH_{0.66} rather than at PdH_{0.55}. If the above explanation is correct, it should be possible to obtain a linear increase in susceptibility as hydrogen is removed from PdH_{~0.66}. This was attempted³ by a high-voltage method for extracting hydrogen without heating the sample and it was claimed that all the hydrogen could be removed without any change in the magnetic susceptibility. These results were not confirmed by Lewis, *et al.*,⁴ using an electrolytic method for removing hydrogen but were partially confirmed in this laboratory⁵ using the high-voltage method.

In the present series of experiments diamagnetic and slightly paramagnetic samples of palladium hydride were prepared from very fine (0.80- μ) palladium metal powder, by alternately heating and cooling the metal in pure hydrogen (obtained by evolution from UH₂), at a temperature which never exceeded 200° above which the powder sinters. These samples evolved hydrogen at room temperature when the hydrogen pressure above them fell below 18 mm. The magnetic susceptibility of samples of palladium hydride was continuously compared to that of a standard (Mohr's salt), while small measured quantities of hydrogen were removed from the sample, in an apparatus which has been described previously.⁶ The results are shown in Figure 1. Curves 1 and 2 show that it is possible to remove a large fraction of the hydrogen from diamagnetic palladium hydride and from palladium hydride which is slightly paramagnetic owing to an initial lower

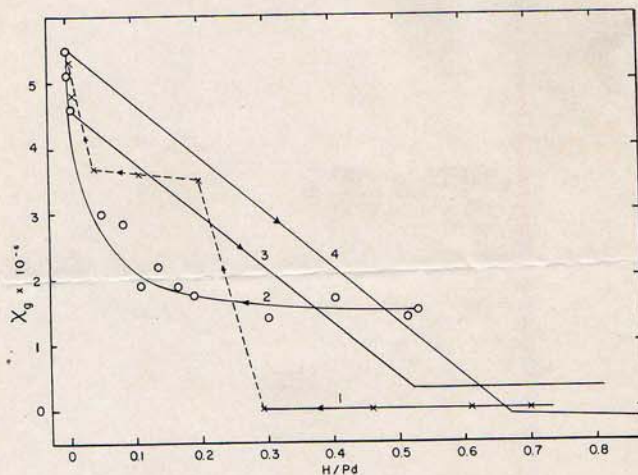


Figure 1. The effect of absorption and desorption of hydrogen on the paramagnetic susceptibility of palladium.

hydrogen content, without changing the susceptibility (χ_g). Curves 3 and 4 for the absorption of hydrogen by palladium are taken from Smith.¹ It thus appears that the band theory explanation is not tenable for the desorption of hydrogen from palladium hydride and it may be that lattice expansion plays a more important role than was formerly thought. Further experimental and theoretical work is in progress.

Acknowledgment. The authors are indebted to the U. S. Atomic Energy Commission for financial support for this work.

- (1) D. P. Smith, "Hydrogen in Metals," University of Chicago Press, Chicago, Ill., 1947.
- (2) N. F. Mott, *Advan. Phys.* **13**, 325 (1964).
- (3) A. Michel and M. Gallissot, *Compt. Rend.*, **208**, 434 (1939).
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- (5) T. R. P. Gibb, Jr., to be submitted.
- (6) W. A. Norder, *Rev. Sci. Instr.*, **31**, 849 (1960).

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RECEIVED JULY 18, 1966