STUDIES OF THE LOW TEMPERATURE ANOMALY IN PALLADIUM HYDRIDE

BY

THOMAS EDWARD ELLIS

B.S., Massachusetts Institute of Technology, 1973
M.S., University of Illinois, 1974

THESIS

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Three studies of the low temperature anomaly in Pd-H and Pd-D have been undertaken. In the first, a study of the electrical resistance anomaly has been made to determine the effects of varying hydrogen concentration. The temperature of the resistive peak was seen to increase with $H(D)/Pd$ for ratios above .63.

In the second experiment samples of Pd-H and Pd-D with high ($T_a > 70$ K) anomaly temperatures have been held below $T_a$ for extended time periods. Resistance was seen to fall by up to 60% after several days of annealing. Reductions in annealing temperature caused further reductions in resistance. The changes are reversible; heating the samples to 90 K or more restored the original resistance.

The third experiment was a neutron diffraction experiment on a single crystal of PdD$_{76}$. Annealing the crystal at 70 K produced superlattice diffraction lines belonging to the star {4/5 2/5 0}. The growth of the new lines with time bears a striking relationship to the resistance behavior. The peaks were erased by heating to 90 K, and reappeared at the same locations when the crystal was again annealed at 70 K.
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I. INTRODUCTION

The ability of palladium to absorb large quantities of hydrogen gas was first reported in 1866.\(^1\) In the following years the palladium-hydrogen system has come to be the most extensively studied of the metal/gas systems.\(^2\) The early literature dealt with studies of solubility, phase diagram and mechanical properties. Industrial interest centered on the use of palladium as a hydrogen purifier, and as a catalyst in hydrogenation reactions.

Recent academic interest in palladium hydride has been stimulated by the discovery of its superconducting properties. Pure palladium is not a superconductor because of its strong paramagnetism. In 1972 Skoskiewicz announced that palladium hydride with an H/Pd atomic ratio of 0.8 or more is superconducting.\(^3\) Other studies, such as that of Miller,\(^4\) showed that the \(T_c\) of the hydride rose with H/Pd ratio, reaching 9K for H/Pd of 1.0. Further, there is a large reverse isotope effect. That is, a sample of palladium deuteride has a higher \(T_c\) than a sample of hydride at the same concentration. This result is the opposite of what is predicted by the BCS theory of superconductivity. The superconducting properties of Pd-H are still a matter of great controversy.

In comparison to the questions raised by its superconductivity, the "low temperature anomaly" in palladium hydride is a minor but annoying puzzle. The anomaly was first detected in 1957 as a peculiar maximum in the specific heat of a Pd-H sample near 55 K. Anomalous behavior in the same temperature regime also appears in the electrical resistivity, internal friction, and Hall constant. Other quantities such as the magnetic susceptibility show no untoward behavior. A complete description of the experimental evidence available is given in Chapter II.
There have been several explanations put forward for this peculiar behavior. All of these explanations suffer from one or more fatal defects. All of these attempts are examined in Chapter II. This inability to solve such an apparently minor puzzle in twenty years gives the problem its annoying quality. The present work is yet another attempt to resolve this embarrassing situation.

This work presents the results of three experiments. The first involved a study of the electrical resistivity anomaly. The objective was to determine the effect of the hydrogen concentration on anomaly temperature. This experiment is described in Chapter III. The results showed that high hydrogen concentration raised the anomaly temperature from 50 K to nearly 80 K. This made it feasible to use pumped nitrogen to study the long term behavior of the resistivity below the anomaly temperature. This "low temperature annealing" experiment is discussed in Chapter IV. The results of this experiment strongly indicated that the anomaly was due to an ordering of the hydrogen into a superlattice.

The third experiment was a neutron diffraction experiment to search for this hydrogen superlattice. The results of this search are presented in Chapter V. These results, while not complete, point the way for experiments which should solve this problem at long last.
II. PREVIOUS WORK

A. Experimental

1. Resistivity

The electrical resistivity has been the most extensively and systematically studied property of the low temperature anomaly. The first such study was reported by Schindler et al. in 1959. They reported that two samples of Pd-H exhibited strong maxima in their ρ curves. One sample with an H/Pd ratio of .54 had the maximum at 52 K; the other sample, H/Pd = .60, had the maximum at 43 K. The authors noted their experimental temperatures were liable to be "several degrees low."

A more systematic study was reported by Ho and Manchester in 1968. They studied several samples of both palladium hydride and deuteride for H(D)/Pd ratios up to .63. The range of temperature covered was 4 to 300 K. For H(D)/Pd ratios above .4 a small peak in the ρ vs. T curves appeared near 53 K. The location of the peak in temperature was independent of H/Pd ratio. For samples allowed to age and lose hydrogen the form of the ρ vs. T curve changed. The resistivity maximum disappeared, replaced by a change in slope of the curve at 53 K. The authors also remarked that the residual resistivity was found "to vary somewhat with the manner in which the alloy is cooled down."

The nature of that variation was reported more fully by Haywood and Verdini that same year. They again observed a peak in the ρ v. T curves for several H/Pd ratios. The new result was how thermal history affected the residual resistivity. A sample quenched from 77 K to 4.2 K had a much lower residual resistivity than it had when it was allowed to cool to 4.2 K
very slowly. $T_a$ was lower for the slow cooled sample than the quenched sample (44 K vs. 52 K). When the slow cooled sample was allowed to warm back to 77 K, no hysteresis appeared in the $\rho$ vs. $T$ curve except very close to $T_a$. The resistivity was also reported to show some time dependence at various temperatures.

Ho and Manchester reported on the thermal history effects and time dependencies in 1969.\(^8\) For a PdD.\(_{0.58}\) sample they reported the $\rho$ vs. $T$ curve consisted of two distinct branches. See Figure 1. For the upper branch, as much as six hours was taken to cool from 80 K to 25 K. The lower branch came from quenching the sample from 80 K to 4.2 K in one minute, and then measuring resistivity while slowly warming the sample. The two branches coincide for $T \geq 52$ K, the $T_a$ of the lower branch. At lower temperatures, the slowly cooled sample had a higher resistivity, the difference reaching 3% at 4.2 K. Below 52 K, the quenched resistivity was time dependent. For fixed $T$, the quenched resistivity increased with time, approaching the value of the upper branch at this $T$. The growth in $\rho$ had a time dependence close to a simple exponential. The time constant in this exponential fitted an equation of the form $\tau = \tau_0 \exp(E/kT)$. For the deuteride, $\tau_0 = .3$ sec and $E = 950$ cal/mole. Further, $\tau_0 (\text{D/Pd} = .58)$ was thirty times larger than $\tau_0 (\text{H/Pd} = .59)$. Annealing the sample at 80 K for a few hours erased the effects of the previous history.

The above studies were made with samples loaded with hydrogen by an electrolytic technique. In 1968 Skoskiewicz and Baranowski reported on a sample made by exposing Pd to very high pressure hydrogen gas.\(^9\) The sample was initially charged to an H/Pd of .89. No peak in the resistivity was seen up to 80 K. The sample was then allowed to lose hydrogen in small
Figure 1. The data of Ho and Manchester showing the effect of cooling rate on the resistivity vs. temperature curves in Pd-H.
D/Pd = 0.58

"slow"

"fast"

p (micro-ohm cm)
decrements. For H/Pd = .74, a resistance peak appeared near 60 K. For H/Pd = .67, \( T_a \) was 57 K. For H/Pd = .58 an inflection, much like that of Ho and Manchester's aged samples, appeared at 53 K. For H/Pd of .49 and less no anomaly was observed. Harper reported similar results in 1974.

Szafranski studied both palladium-hydrogen and palladium-silver-hydrogen alloys. For Pd\( \text{H}_x \), he reported a \( T_a \) of 50 K for \( x \) up to .60. For higher \( x \), \( T_a \) increased steadily, reaching 85 K for H/Pd = .85. As \( x \) increased the size of the resistive peak decreased. Adding silver to the palladium rapidly destroyed the anomalous behavior.

Finally, MacLachlan et al. studied the resistivity of an H/Pd = .995 sample. They observed no resistivity anomaly whatever.

2. Specific Heat

Nace and Aston are credited with the discovery of the low temperature anomaly in 1957. They were studying the specific heat of palladium black with H absorbed to form an H/Pd of .49. A plot of \( \Delta C_p(T) = C_p(T)_{\text{Pd}} - C_p(T)_{\text{PdH}} \) showed a sharp maximum near 55 K. A sample loaded with deuterium to D/Pd = .48 showed a larger maximum at 57.5 K.

In a later paper Mitacek and Aston measured the heat capacities of solid specimens with H/Pd ratios of .125, .25, .50, and .75. Again, plotting \( C_p(T) \) gave sharp peaks near 55 K. When \( C_p(T) \) per mole absorbed H was plotted, it was found that the data from all four samples fell on the same curve.

Jacobs and Manchester did a careful study of the specific heat of an H/Pd = .63 sample. Their results showed that the size and shape of the specific heat peak depended on the rate at which the sample was heated in the region of \( T_a \). A smaller heating rate gave a larger peak, but the position of
the peak in $T$ did not change. See Figure 2. For temperatures both much
higher and much lower than 55 K the measured specific heat was essentially
independent of heating rate.

One other interesting phenomenon has been reported from specific
heat measurements. Fritz, Maria, and Aston found\textsuperscript{16} that samples of
$H/Pd = .5$ cooled to less than 1 K showed a spontaneous temperature rise be-
yond normal heat leaks. Samples slowly cooled from 77 K to 4.2 K showed a
much lower spontaneous heating than samples quenched to 4.2 K. Mackliet
and Schindler strengthened the connection of this effect to the anomaly.\textsuperscript{17}
They found that the amount of heat evolved could be greatly reduced by "annealing" at 50 K for several hours before cooling to 1 K. The spontaneous
heating power decayed exponentially with time following initial cooldown to
4 K. For similar thermal histories the spontaneous power decreased with in-
creasing $H/Pd$ ratio. See Figure 3. Raising the sample temperature to 77 K
for as little as half a day "erased" the effects of previous thermal history.
This last result indicated the heat evolved was not due to any irreversible
change in the samples.

The early heat release experiments were done at very low temperatures.
This was necessary because the spontaneous power is very small. Only at
very low temperatures were the heat capacities of sample and holder small
enough that this small heat release produced a measurable temperature rise.
In 1977, Jacobs and Manchester succeeded in measuring the heat release near
50 K.\textsuperscript{15} Their results showed the time dependence of the spontaneous power
was that of a sum of two exponentials. The amount of power that could be
ascribed to each exponential was temperature dependent. The faster com-
ponent (smaller time constant) dominates at very low temperatures and for $T$
Figure 2. The specific heat anomaly and the effect of different heating rates. From Jacobs and Manchester.15
Figure 3. The decay of the spontaneous heating power in Pd-H. Note the decrease in heating power at high H/Pd ratios. From Mackliet and Schindler.
above 48 K. Between 40 and 48 K the slower component dominates. Both time constants depend on temperature like a thermally activated process, i.e.,
$$\tau_{f,s} = \tau_0 \exp(E/\beta)$$
Both time constants appeared to have the same activation energy \(E\), differing only in the pre-exponential factor. The ratio of either time constant for a deuteride sample relative to the equivalent for the hydrogen sample was 1.40. This result implied that hydrogen diffusion was involved in the process.

3. Internal Friction

The internal friction of a material is a measure of its inelasticity. This inelasticity originates in defects such as vacancies and grain boundaries in the material. One standard method of measurement is to make the sample to be studied the spring in a harmonic oscillator. A torsion pendulum is the most frequently used system. By measuring the resonant frequency and decay time of the oscillator the internal friction can be calculated.

In metal hydrides internal friction measurements can be very revealing. A non-saturated hydride can inelastically relax a stress by having hydrogen atoms jump to new sites in the lattice. One standard technique is to fix the oscillator frequency and vary the sample temperature. A peak in the internal friction will occur at a temperature at which the pendulum frequency is the same as the hydrogen jump frequency. By measuring at several different pendulum frequencies the hydrogen diffusion constant as a function of temperature can be determined.

Zimmerman first reported internal friction measurements on Pd-H alloys in the 50 K region. His results showed that the slope of the internal friction vs. \(T\) curve changed discontinuously near 50 K. The discontinuity became broader and moved to higher temperature with increasing H/Pd ratio.
In fact, the author plotted his results for the rise in $T_a$ he saw and compared them with what other authors had reported for the resistivity anomaly. The data from the different experiments all fell on the same curve.

A more complete investigation was reported by Jacobs et al. They performed measurements using a torsion pendulum which operated at much lower frequencies than that of Zimmerman. Instead of a slope change they observed a peak in the internal friction near 50 K. The $T_a$ of this peak did not change when the pendulum frequency was changed. The magnitude of the peak did change, decreasing rapidly with increasing frequency. The authors claim this explains the difference between their data and that of Zimmerman.

The magnitude of the internal friction depended on thermal history in the vicinity of $T_a$. As one example, a sample held at 47 K for several hours before cooling to 4.2 K was compared to its behavior when rapidly quenched from 77 K to 4.2 K. The slow cooled sample had an internal friction 20% lower than the quenched sample. This sample was also subjected to a step change in temperature from 47 to 48 K. The internal friction rose rapidly at first, and then began to slowly decay back to its original value.

As a final test, a sample was first cooled to 60 K and then slowly warmed while measuring the internal friction. The sample was then cooled to 50 K and warmed and measured again. The internal friction curves were essentially identical above 60 K. This indicates that, like the spontaneous heating, whatever causes this internal friction is not causing a permanent change in the sample.

4. Hall Constant

The anomaly has also been measured in the Hall constant. Zepeda and Manchester measured the Hall constant in two Pd-H samples and one Pd sample.
In the hydride samples, the slope of $R_H$ vs. $T$ changed near 50 K. See Figure 4. One sample quenched below this temperature showed a change of $R_H$ with time. The time constant for this change was on the order of 5000 minutes. The authors noted that this was an order of magnitude larger than the time constants seen in resistivity studies.

5. Other Studies

There have been several other studies attempting to find anomalous behavior near 50 K. With one possible exception, all have been negative.

Three studies of the magnetic susceptibility in the 50 K region have been reported. Jamieson and Manchester tested samples of Pd-H and Pd-D for concentrations up to .71. The temperature range was 4.2 to 300 K. For concentrations up to .41 a very broad peak centered at 85 K and nearly 40 K wide was observed. The authors stated they did not believe this hump was in any way connected to the 50 K anomaly. This conclusion was reinforced by the total absence of any hump in the .61 and .71 samples. Resistive anomalies are quite evident at these concentrations. The results of Miller were similar. No anomalous behavior of the susceptibility was observed in the range of temperature where the anomaly usually occurs.

A different result was reported by a Russian group in 1977. This group saw a sudden change in the slope of $\chi$ vs. $T$ near 50 K for samples with H/Pd ratios of .59 and .65. No explanation was given as to why this group obtained results different from those cited above.

One study has been reported on the effect of temperature on the Raman spectra of Pd-H(D). Samples of PdH.79 and PdD.75 were studied. In both cases no major changes were seen in the Raman spectra on cooling through the anomaly region.
Figure 4. The data of Zepeda and Manchester$^{20}$ showing the low temperature anomaly in the Hall Constant.
One X-ray diffraction study of Pd-H near 50 K has been reported. This study was sensitive to the palladium atom positions only, due to the low scattering cross section of hydrogen. Three different H/Pd ratios were used, and the samples were subjected to several kinds of thermal history. No anomalous behavior of any kind was detected. No changes were seen in the crystal structure or lattice constant, and no line broadenings indicative of lattice strains were visible.

Several neutron scattering experiments have been performed at low temperature. These will be discussed in the second half of this chapter.

Finally, a very recent study of the elastic constants of PdH$_{1.66}$ has been reported. This study observed no anomalous behavior of $C_{44}$ in the low temperature region.

B. Theoretical

There have been several explanations advanced for the low temperature anomaly since its discovery. They range in sophistication from simple claims of a new phase being formed to detailed calculations of anomaly temperature based on this or that theory. Most of these explanations are more properly labeled models than theories. All of them are either demonstrably incorrect or have serious problems. The following will catalogue these models and list the shortcomings of each.

1. PdH$_4$ Rotation

This model was proposed by Nace and Aston when they discovered the anomaly and was modified in later papers by Aston. Aston noted that the specific heat anomaly is similar to that seen in covalently bonded molecules such as CH$_4$ in the temperature region where rotational modes of the
molecule are excited. In its original form, this model proposed that \( \text{PdH}_{0.5} \) consisted of quasi-molecular tetrahedral \( \text{PdH}_4 \) units scattered through the Pd lattice. Below 55 K these molecules were "frozen." Near 55 K the units would become free to rotate and absorb energy. This would cause the observed peak in the specific heat.

The original model was discarded when neutron scattering studies showed that the hydrogen atoms are located in the octahedral interstitial sites, not the tetrahedral sites as proposed. (See Appendix A.) In its new version, the model assumed planar \( \text{PdH}_4 \) units lying in the (100) plane of the Pd lattice. For the composition \( \text{PdH}_{0.5} \), the (100) planes would be saturated with hydrogen while the (200) planes would be hydrogen free. Near 55 K the atoms would become free to move to equivalent positions in the same plane by a ring diffusion mechanism. This would be equivalent to a rotation of the \( \text{PdH}_4 \) units. The energy absorbed in exciting this rotation would produce the specific heat peak. The resistivity anomaly was assumed due to changes in the electron-phonon scattering as the H atoms moved. To account for the spontaneous heating, it was proposed that quenched Pd-H would have some \( \text{PdH}_4 \) units frozen into planes other than the (100) planes. These units would slowly diffuse back into the (100) planes. In so doing, they would lower their energy, the difference showing up as the spontaneous heat evolved.

This model has several serious flaws. The structural studies that have been done show the structure assumed in this model does not exist. The model is unable to explain the rise in anomaly temperature with H/Pd ratio or the time dependencies seen in the resistivity and internal friction. Nor is the model capable of explaining the dependence of the magnitude of the specific heat on heating rate. Given these failures, it is little wonder that this
model has been completely ignored in the literature published since 1963.

2. Octahedral to Tetrahedral Site Migration

This model was proposed in 1965. For several years it was accepted as the correct model for the anomaly, despite several serious flaws. The disproof of this model left a gap which no other model has come close to filling.

Early neutron diffraction studies showed that at room temperature Pd-H has an FCC crystal structure like that of NaCl. The H atoms occupy the octahedral interstitial sites (with coordinates $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) in the Pd lattice. See Appendix A. Working with a sample of PdH, Schindler et al. conducted similar studies at 77 K and 4.2 K. They observed no new diffraction peaks nor any drastic changes in the scattering angles of the existing peaks. They did observe changes in the intensities of the diffraction peaks unlike what they had expected. To explain these results they postulated a change in the crystal structure.

Schindler et al. interpreted their neutron data as indicating that below 55 K the H atoms migrate from the octahedral sites to the tetrahedral sites (coordinates $1/4,1/4,1/4$ and $3/4,3/4,3/4$). A slight trigonal distortion of the Pd lattice should accompany this migration. Working with the structure factors for such a system, the authors calculated a fit to their data that showed approximately one H atom per unit cell in the tetrahedral sites.

This model did appear to explain several of the observations on the anomaly. The migration of the H atoms would cause a change in entropy which could give the specific heat peak. The resistivity peak came from the extra scattering that resulted when the H atoms moved between sites and created a
highly disordered system. Quenched material would not have the equilibrium number of H atoms in the tetrahedral sites. The slow diffusion of H atoms into these sites would then explain the spontaneous heating and the various time dependencies that had been seen.

Several problems with this theory were noted in the years before it was finally disproved. First, the authors fit their data using scattering factors which implicitly assume an H/Pd ratio of 1.0, not the .66 sample they used. Thus the closeness of the fit between their observed intensities and the intensities they calculated seems in retrospect to be accidental. It should also be noted that if such a site migration took place, the H atoms in the tetrahedral sites would form an ordered superlattice. This superlattice should cause extra diffraction peaks to appear where none were seen in the high temperature data. No such extra lines were detected. The authors stated that the sensitivity of their apparatus was not good enough to permit detection of such lines. In addition, it proved difficult to explain the rise in $T_a$ with H/Pd and the simultaneous decrease in the magnitude of the anomaly. Szafranski and Baranowski made an attempt to explain these two problems, but their proposal requires some tetrahedral site occupation even at high temperature, in direct contradiction to the neutron observations. Furthermore, several calculations of the energy band structure of Pd-H showed the octahedral sites to have a lower H occupation energy than the tetrahedral sites at all temperatures. A study of the residual resistivity came to the conclusion that the H atoms could only be located in the octahedral sites at low temperatures. Lastly, it was pointed out that the time constants observed in the resistivity were many orders of magnitude larger than such a model would predict.
This model was finally disproved by two new neutron scattering studies. Entin et al. first reported a study of PdD$_2$. By using deuterium instead of hydrogen, the sensitivity of this experiment to superlattice lines was greatly enhanced. On cooling from 300 K to 4.2 K they observed new diffraction peaks, but in locations expected for an FCC structure, not a tetrahedral structure. These new peaks were interpreted as precipitates of the low concentration alpha phase of Pd-H. Such a precipitation could be expected for such a concentration cooled in such a manner (see Appendix A). The authors computed the remaining beta phase to have a D/Pd of .63 which later results have shown to be correct. The authors were able to fit their data by assuming the observed lines came from the alpha and beta phases and assuming only octahedral site occupation in both phases. In addition, the authors state no deuterium superlattice were seen.

Mueller et al. performed neutron scattering studies on both hydride and deuteride samples with H(D)/Pd ratios from .60 to .92. These ratios assured no precipitation of the alpha phase. The conclusion of this study was that the H(D) atoms were located in the octahedral sites only for all temperatures and compositions.

3. Hydrogen Clustering

This model presupposes the existence of an attraction between H atoms in the Pd lattice. Given such an attraction the H atoms will tend to congregate in clusters at low temperature. At high temperature thermal vibrations overcome the attraction and causes the clusters to disperse.

Brodowsky proposed this model in 1972. He began by trying to explain the miscibility gap in the Pd-H phase diagram (See Appendix A). It was pointed out that such a gap could be caused by an attraction between H
atoms. From phase diagram data Brodowsky worked out the magnitude of this attraction, and from it the binding energy of an H-H pair. He then noted that at high temperature the number of H-H pairs should be that of a random distribution of hydrogen throughout the palladium lattice. This would be the minimum number of pairs possible and would be unchanged by a small change in temperature. At very low temperature the H atoms should form clusters of nearly stoichiometric PdH with a maximum number of pairs. Again a small change in temperature would not affect the number of pairs. At some intermediate temperature the number of pairs changes from a maximum to a minimum. In this region the number of pairs is strongly T dependent. This change in pair number will lead to a specific heat peak in this temperature region. A rapidly cooled specimen would not reach equilibrium but have a large amount of disorder frozen in. As time passed and H atoms slowly diffused, they would form pairs and liberate their bonding energy as the spontaneous heat. This model made no attempt to explain the resistivity data.

This theory failed when calculations of specific quantities such as anomaly temperature were attempted. These calculations concluded that \( T_a \) should be greatest for H/Pd = .50 and should decrease for higher hydrogen contents. This result is contradicted by the resistivity and internal friction data described earlier. In addition both the magnitude and breadth of the calculated specific heat anomaly were in total disagreement with the measured data.

Stafford and McClellan\(^{37}\) did a detailed statistical mechanical treatment of the clustering problem, again assuming an attraction between hydrogen nearest neighbors. They specifically criticized Brodowsky for using an inadequate treatment. The specific heat peaks derived in this paper are an
order of magnitude smaller than the experimental ones. In addition, $T_a$ turns out to be independent of $H/Pd$ ratio, again contrary to experiment.

4. Other Models

Jacobi and Vaughn proposed a simple Schottky anomaly as a model for the specific heat results. They postulated that Pd-H contained several energy levels coupled by Boltzmann statistics. The authors made a point of refusing to identify or even speculate as to the nature and cause of these energy levels. The specific heat anomaly occurred when the high energy levels became appreciably populated. As with other models this one gives a $T_a$ independent of $H/Pd$. The authors themselves point out the calculated specific heat peak is much broader than experiment.

Boureau and Kleppa proposed the anomaly was caused by a displacement of the Pd atoms. Such a displacement has not been seen in the X-ray study noted above or the neutron scattering studies. 34,35

Jacobs and Manchester have suggested that H atoms in Pd-H can be treated as a lattice gas. The low concentration alpha phase represents the gas, the beta phase is then a lattice liquid. Tha authors then postulated a new and as yet unseen gamma phase to represent the solid form of the lattice gas. They then suggested the anomaly was due to the beta-gamma phase transition. But the authors failed to give any of the properties of this new phase. They failed to show why it forms or how its formation would explain any of the experimental data. As such this model is so general that it is impossible to verify. This model merely describes the anomaly without explaining it.
III. ANOMALY TEMPERATURE MEASUREMENT

When this experiment was begun, there had been no comprehensive study of the dependence of $T_a$ on H/Pd ratio. At present one such study has been reported using internal friction measurements (See Chap. II, Sec. A 3). The studies of the resistivity anomaly are still fragmented however. This experiment represents the first attempt to study the resistive anomaly across the entire range of H/Pd in which it is found.

A. Apparatus

The experimental apparatus is shown in Figure 5. This device consisted of two concentric stainless steel tubes. The outer tube served as a vacuum jacket to isolate the sample and holder from the surrounding liquid helium bath. In addition, the end plate of this jacket held the reference junction for the sample thermometer (see below). With the inner tube in position, a vacuum seal was made by an O ring and screw cap arrangement.

The inner tube served as a carrier for the copper sample holder. The electrical leads for the experiment ran inside this tube and out through an epoxy seal at the top. The lower end terminated in a copper end cap. This end cap contained a threaded screw hole to receive a matching screw on the sample holder. A manganin wire heater was wound inside the end cap. The electrical leads came through holes in the cap, which was then sealed with epoxy. See Figure 6a.

The sample holder is shown in Figure 7. It was machined from a single block of copper to eliminate temperature variations along the sample. The sample and contact holders rested in a channel 1/4 inch wide. This channel was insulated with cigarette paper soaked in G.E. 7031 varnish.
Figure 5. The apparatus for measuring the electrical resistance anomaly. The two tubes, sample holder, and thermocouple spiral are visible. This drawing is not to scale.
Figure 6. (a) A cross sectional view of the copper end cap on the inner tube. (b) A cross sectional view of the sample holder, showing the spring-contact holder - sample arrangement.
HOLES FOR WIRES
MANGANIN HEATER
SCREW HOLE
INTERIOR SPACE EPOXY SEALED

STAINLESS STEEL TUBE
COPPER END CAP

UPPER PART OF SPRING
SAMPLE HOLDER

CLAMPING SCREW
CONTACT HOLDER
CONTACT
SAMPLE
Figure 7. The sample holder.
Experience with this combination has shown it provides good electrical isolation of the sample while allowing good thermal contact between sample and holder.

Sample resistance was measured by a conventional four probe DC technique. Contacts to the sample were made by thin copper plates held on edge in teflon contact holders. Good electrical contact was insured by pressing on the holders with a Be-Cu spring. Figure 6b shows a cross sectional view of the arrangement. In practice, a nylon spacer was put between the two teflon pieces and the holders butted firmly against it before being clamped down. This insured a reproducible spacing between the voltage probes.

The primary thermometer used for the experiment was a gold + 7 atomic percent iron vs. copper thermocouple. This particular combination was chosen because of the good sensitivity and large output voltage in the 40 to 90 K temperature region. The thermocouple was referenced against the surrounding liquid helium bath. To accomplish this a spiral coil consisting of the thermocouple wires, a piano wire wound as a spring, and a fiberglass sheath, ran from the sample holder to the end plate of the vacuum jacket. The copper and gold wires were spot welded to form the reference junction. The junction and spring were then soldered into a hole in the end plate. At the other end, the spring was attached to the end of the sample holder with a screw. The gold wire was spot welded to another copper wire to form the measurement junction. This junction was epoxied into a hole in the end of the sample holder for thermal contact. This arrangement of the thermocouple coil allowed the sample holder to be removed from the outer jacket for sample changes. With the holder inserted into the jacket, the coil contracted out of the way of the holder.
Figure 8. Block diagram of the electronics used in the measurement of anomaly temperature.
The thermocouple was calibrated against a germanium resistance thermometer. This thermometer was factory calibrated from 1.5 to 100 K. The thermometer was sealed into a hole in the sample holder with a small amount of Apiezon N grease.

The electronics for this experiment are shown in a block diagram in Figure 8. A DC power supply fed current to the sample through a variable resistor and a 100 ohm precision resistor. Measurement of the voltage across the precision resistor by a digital voltmeter allowed determination of the sample current to better than one part in ten thousand. Sample resistive voltage was detected by a Keithley nanovoltmeter. The output voltage of this instrument drove the Y axis of an X-Y recorder. The voltage across the thermocouple was sensed by a second nanovoltmeter whose output drove the X axis of the recorder. The result was a plot of resistive voltage vs. temperature.

B. Sample Preparation and Characterization

Samples were prepared from .002" thick Pd foil supplied by the Materials Research Corp. Spectrographic analysis performed by the Chemical Analysis Group at the Materials Research Laboratory here at the University of Illinois gave an overall purity of 99.97% Pd. The major impurities were Si and Al. The foil was cut into strips .2" wide and 1.75" long. The strips were degreased, etched in a dilute HNO₃ solution, and then annealed. There is considerable disagreement in the literature as to the best method for annealing Pd for resistivity studies. The method we used was to anneal the strips at 800 C in vacuum for several days, followed by a slow cooldown to room temperature. This procedure gave a residual resistance ratio of 70 in the annealed foil, compared to an as received value of 18.
Several methods were used to charge the samples with hydrogen. Most of the samples were prepared by an electrolytic charging method described by Miller. For samples with H/Pd ratios up to .8 the charging could be carried out at room temperature. For higher ratios the charging cell was held at -78 C. Experience showed that samples produced by this method did not have the hydrogen distributed uniformly through the foils. The resistivity vs. T curves for these foils were characteristic of nearly pure Pd, indicating that most of the absorbed hydrogen was still at or near the surface immediately after charging. To overcome this problem samples were stored after charging in a dry ice - acetone bath for several days. At this temperature (-78 C) hydrogen has a reasonably high diffusion constant in Pd. The H atoms could thus diffuse through the foil and form a homogeneous distribution. At the same time, this temperature is low enough to prevent hydrogen desorption, which is a problem at room temperature.

A few samples were produced by the direct reaction of the Pd with hydrogen gas. For ratios less than .6 the foils could be charged in low pressure (several psi) of gas. For high concentrations the samples were charged in the high pressure hydrogen apparatus developed in our laboratory for investigations of thorium hydride. In this apparatus samples could be charged at pressures up to 20,000 psi. This procedure lent itself to the production of strain-free samples, as the foils could be charged in a fashion that prevented the samples from ever entering the two phase region of the phase diagram. Both of the direct reaction methods had the advantage that hydrogen was uniformly distributed through the samples after charging. The main disadvantage was that we had very little control over the resulting H/Pd ratio. We were unable to detect any differences between samples of similar
composition made by different methods.

The H/Pd ratio of each sample was determined after resistive measurements on it were completed. The method used was a volumetric determination. This method has been described in detail elsewhere \(^{22}\) so only a brief description will be given here. The sample to be measured was loaded into a quartz furnace tube which was then evacuated. The sample was then heated to 450 °C to drive off the hydrogen. The evolved hydrogen gas was forced by a series of pumps into a known volume connected to a sensitive pressure gauge. Measurement of the pressure of the evolved gas gave the number of moles of H that had been in the sample. Weighing the now desorbed foil gave the amount of Pd in the foil, and from this the H/Pd ratio was calculated.

C. Resistance Measurement

Palladium hydride is unstable against hydrogen loss at room temperature. To prevent H loss all samples were loaded into the sample holder while the holder was held in a liquid nitrogen bath. The holder was then inserted into the vacuum jacket and the whole rapidly put into a LN\(_2\) bath. With practice, the holder could be prevented from ever rising above 150 K, which provided an adequate safety margin.

We were able to produce both "slow" and "fast" cooling curves similar to those of Ref. 8. "Fast" curves were obtained for all the samples studied. The quenching was accomplished by filling the vacuum jacket with helium gas while the entire assembly sat in LN\(_2\). The assembly was then taken from the LN\(_2\) dewer and plunged directly into a cryostat full of liquid helium. The temperature of the sample holder fell to 40 K within four minutes and reached 6 K in six minutes. Heat leaks in the apparatus prevented the holder from reaching lower temperatures. The sample holder was warmed by first slowly
pumping out the helium from the vacuum jacket and then slowly increasing the current in the sample heater. Heating rates below 30 K were usually 1 to 2 degrees per minute, while above 30 K the heating rate could be held to .4 °K/min.

A few samples were also studied with "slow" cooling. To accomplish this the vacuum jacket was pumped to a hard vacuum with the holder at 77 K. The assembly was then put into a liquid helium filled cryostat. Extremely small amounts of helium gas were admitted into the vacuum jacket, creating a weak link to the bath that slowly cooled the sample. Cooling rates of \( \frac{1}{2} \) °K/min could be obtained by this method.

An appreciable zero-current voltage appeared across the voltage leads at low temperature. This voltage was undoubtedly due to thermoelectric effects in the electrical leads and connections. To eliminate this problem, the sample current was periodically removed and the zero-current voltage marked on the X-Y plot. This was done every 25 microvolts of thermocouple voltage for \( T < 45 \) K (roughly every 1.5 degrees) and every 12.5 μV for higher temperatures. The difference between the voltage seen with current and the zero-current voltage was then taken as the true resistive voltage.

D. Results

Plots of resistive voltage vs. temperature for several samples are shown in Figures 9 through 18. At the lowest \( H/Pd \) ratios the sample resistance after quenching is a nearly linear function of \( T \). At slightly higher concentration (Fig. 10) a broad enhancement above the straight line increase is seen. The center of this enhancement is taken to be \( T_a \). For even higher \( H/Pd \) the curve breaks into two straight lines with different slopes (Fig. 11). The point at which the slope changes is now taken to be \( T_a' \). As the hydrogen
Figures 9 - 18. Plots of resistive voltage vs. T for several Pd-H and Pd-D samples. The small arrows indicate the temperature taken to be $T_a$. 
Figure 10.
Figure 11.
# 11  \( H/Pd = 0.502 \)

\( I = 12.50 \text{ mA} \)
Figure 12.
#16  H/Pd = 0.572

I = 10.00 mA

\[ V_R (\mu V) \]

\[ \text{Temperature (K)} \]
Figure 13.
# 18 H/Pd = .634

I = 7.50 mA

- quench

+ slow cool
Figure 14.
#72  D/Pd = 0.698

I = 60 mA

$V_R (\mu V)$ vs Temperature (K)
Figure 15.
#78  H/Pd = .762

I = 70 mA

$V_R (\mu V) - Temperature (K)$
Figure 16.
#64 H/Pd = 0.819
I = 6.80 mA

- quench
- slow cool
#66  H/Pd = 0.885
I = 70 mA

\[ V_R(\mu V) \]

Temperature (K)
Figure 18.
concentration is increased the change in slope becomes more pronounced (Fig. 12). Finally a full-fledged resistance maximum appears (Fig. 13). Figure 13 also shows the difference in resistance curves between "slow" cooling and "quenching." Above the quenched peak the two curves are identical within the experimental uncertainty. The peak in the slow cooled data is very broad and several degrees lower than the quenched peak. At low temperatures the slow cooled resistance is 3% higher than the quenched resistance.

At H/Pd ratios above .63 the resistance peak becomes smaller in magnitude (Figs. 14-17). A distinct shift to higher $T_a$'s is seen. At very high concentrations the anomaly appears as a small bump at the end of a long linear region (Fig. 17). For several degrees following the bump the resistance is nearly flat. For the very highest concentration measured the anomaly has again disappeared. The $R$ vs. $T$ curve is again a straight line with no significant distortion up to 93 K (Fig. 18).

The effect of different heating rates on the measured $R$ vs. $T$ curves can be seen in Fig. 19. For higher heating rates the anomaly broadens out and shifts to higher temperature. This should be compared to the effect seen in the specific heat anomaly (Fig. 2) where the peak did not shift. Our measurements of $T_a$ were taken using a rate of .4 °K/min in the region of interest. For the sample shown in Fig. 19 the difference in $T_a$ between this rate and the very slowest rate was about .7 K. Since the breadth of the peaks and variations in quenching rate produce an uncertainty of 1 degree, this discrepancy is tolerable.

The complete plot of $T_a$ vs. H(D)/Pd ratio is shown in Fig. 20. For ratios below .63, i.e., in the two-phase region of the phase diagram, $T_a$ is
Figure 19. Effect of heating rate on the R vs. T curves. The $T_a$ each rate gives is indicated by arrows at the top of the figure.
Figure 20. Anomaly temperature as a function of
H(D)/Pd ratio.
virtually independent of concentration. For ratios above .63, $T_a$ rises rapidly with H content. This implies that the anomaly involves a transformation in the beta phase. The anomaly temperature rises when the beta phase concentration increases, but that ratio does not change with overall sample ratio until the .63 concentration is surpassed.

With $T_a$'s in the 70 to 80 K range it became possible to hold samples below $T_a$ using pumped nitrogen instead of liquid helium. This made it possible to study the time dependencies for much longer time periods than had been done previously. In addition, the use of higher temperatures meant the time dependent effects should occur more rapidly than at the lower temperature that had been used. We therefore began the experiment described in the next chapter.
IV. LOW TEMPERATURE ANNEALING

A. Apparatus

Figure 21 shows the apparatus used to study the resistance vs. time behavior of Pd-H below $T_a$. The samples were on a copper sample holder inside a six inch long stainless steel can. This can served as a vacuum jacket to isolate the samples from the surrounding bath when necessary. The can seated against a stainless steel plate and was sealed with an indium O ring seal. The upper plate held a feed-through for electrical leads and a pumping line through which the can could be evacuated.

Figure 22 shows the copper sample holder. This holder was of the same basic design as the anomaly temperature sample holder. As this experiment was intended to sit at one temperature for extended periods of time a germanium resistance thermometer was the only temperature sensor in the probe. A manganin wire heater was wound on the back of the sample holder.

One difference in this holder was the manner in which electrical contact was made to the samples. A two inch long plate of thin copper was cut to fit inside the central channel. This plate and the channel were insulated with cigarette paper soaked in varnish. Copper wires were then laid along the plate and attached with varnish. The ends of the wires were stripped of insulation, bent to cross the plate, and attached to the plate. Figure 22b shows the arrangement when two samples were to be annealed simultaneously. The amount of time necessary to "anneal" a sample made it desirable to anneal two samples simultaneously. To do this, a good electrical and mechanical joint was made between the two foils. The joint was positioned between the contacts V2 and V3. The foils were now pressed against the plate and contacts by a teflon block and a set of Be-Cu springs similar
Figure 21. The low temperature annealing apparatus.

The plastic fill line extender went to the bottom of the cryostat and allowed the cryogen in the dewar to be flushed out when necessary.
Figure 22. (a) The copper sample holder. The thermometer was sealed into a hole in the copper with Apiezon grease. (b) The plate for electrical contacts. The wire ends going across the plate were free of insulation. This plate fit inside the channel of the holder.
HOLE FOR GERMANIUM THERMOMETER

INTERIOR CHANNEL 1/4" WIDE x 7/16" DEEP

LEADS

I2
V4
V3
V2
VI
II

INSULATED COPPER SUBSTRATE
to those in the earlier apparatus. Contacts I1 and I2 supplied current to the samples. V1 and V2 sensed the resistive voltage of one sample while V3 and V4 served the other sample.

The electronics are shown in Figure 23. The current supply was the same one used in the measurement of anomaly temperature. Resistive voltage was detected by a Honeywell six dial potentiometer. This potentiometer was able to handle two voltage inputs; a selector switch chose which one was actually being measured at a given time. A nanovoltmeter served as the null detector for the potentiometer. The apparatus was accurate to .01 microvolt out of a signal of a hundred microvolts.

A standard four wire measurement was used to detect the resistance of the germanium thermometer. Resistive voltage was detected by a nanovoltmeter whose output was displayed on a digital voltmeter. This combination allowed sample temperature to be determined to within .1 °K, quite sufficient for this experiment.

The sample was maintained at the desired annealing temperature by a pumped liquid nitrogen bath. A pressure regulator designed to control a liquid helium bath was found to work quite well on liquid nitrogen. With the use of the equation of state for liquid nitrogen it was possible to set the desired pressure and thus achieve the desired bath temperature. This technique worked even for bath temperatures below the triple point of nitrogen (63.15 K) where the nitrogen became solid. We were able to maintain sample temperature to ± ½ °K for days between replenishments of the bath. Refilling the bath necessitated lowering the sample temperature to insure the sample would not rise above the desired temperature during refilling and pumpdown. Helium gas in the vacuum can provided a thermal link between the samples and
Figure 23. The electronic arrangement for the low temperature annealing experiment.
D-C SUPPLY → VARIABLE RESISTORS & REVERSING SW. → PRECISION RESISTOR → SAMPLES

DVM

POTENTIOMETER

NULL DETECTOR
the bath. When necessary, the sample could be isolated from the bath by pumping the helium from the vacuum can. This was done during temperature changes and bath refills.

To avoid loss of hydrogen from the samples it was again necessary to load the samples while the holder was held at liquid nitrogen temperature. After the specimens were in place the vacuum can was clamped into place and evacuated. The entire apparatus was then placed in liquid nitrogen and allowed to come to equilibrium. It was again possible to accomplish this without the samples ever warming to more than 150 K. After the apparatus had cooled, the sample heater was used to raise the sample temperature to 95 K and hold it for at least 24 hours. This eliminated the possibility of any prior annealing and provided a reproducible starting point.

The annealing was begun by first quenching the samples from 95 K down to 4.2 K. This was done by filling the cryostat with liquid helium, and then turning off the heater and admitting helium gas into the vacuum can. Due to the large heat capacity of the holder, it took 25 minutes for the samples to cool to 4.2 K. At this point the resistance of the samples was measured.

The sample was now warmed to the desired annealing temperature. The helium was pumped from the vacuum can, and the liquid helium flushed from the cryostat. Liquid nitrogen was then put into the cryostat and pumped down to the desired temperature. During this time the sample temperature would slowly rise to about 40 K. Experience showed this temperature was too low to permit any appreciable annealing in the time involved (about 15 minutes). Helium was now readmitted to the can. This caused the temperature
to rise to that of the bath in about 10 minutes.

Zero-current voltages were again a problem at low temperatures. In this experiment they were eliminated by measuring sample resistance with both forward and reverse sample current. Each point of the data represents the mean of several measurements taken over a 15 minute interval. Standard deviations from the mean were usually less than one part in a thousand.

B. Results

In this section we will present the results of several low temperature annealing runs. A few words about the histories of these samples are necessary first. The first sample to be studied (Fig. 24) was annealed at 70 K but quenched to 4.2 K for resistance measurements. It is possible that the repeated quenchings and rewarmings are responsible for the long annealing time seen in this sample compared to the other samples studied. All the other samples were measured at the annealing temperature. After annealing for 550 hours the sample was heated to 90 K for 24 hours. The sample was then requenched and annealed at 70 K for a short time. The sample followed the same R vs. time curve after this treatment.

The samples in Figures 25 and 26 were run simultaneously. Between the 70 K and 74 K runs the samples were heated to 90 K for 24 hours, and quenched as before and annealed at 74 K. The samples in Figures 27 and 28 were also run simultaneously.

Finally, Figure 29 shows the annealing curve of the single crystal sample used in the neutron scattering experiment described in Chapter V. The very low resistance of this sample is due to its large cross sectional area (a 3/8" diameter cylinder compared to the .002" thick foils). The
quenching done in the second run was intentionally done more slowly than the first run. For the second run the sample was not cooled to 4.2 K first, but was instead cooled from 95 K to 70 K directly. This was done to simulate as closely as possible the technique and cooling rate that was used in the scattering experiment.

The resistance vs. annealing time curves shown in Figs. 24, 25, 26, 27, and 29 show the following features: 1) An initial small increase of R with time in some samples. This is reminiscent of the behavior seen by Ho and Manchester at lower annealing temperature.\(^8\) The lack of this increase in most of the curves may be due to temperature effects or differences in quenching rate. 2) A time period where the resistance is essentially constant. This is followed by 3) a sharp drop of resistance with time. Finally, 4) the R vs. t curve flattens out and R becomes nearly constant again. However, in none of the samples measured did R ever become completely constant in time.

This pattern is not followed by the sample shown in Figure 28. This sample has R constant in time except for an early period when the temperature was slowly rising towards 74 K. (The pressure regulator was malfunctioning and causing T to be too low.) This sample showed no resistance anomaly as can be seen in Fig. 18. This indicates that the annealing behavior seen in the other samples is tied to the anomaly in some fashion.

Figures 25 and 26 show the results of annealing at two different temperatures. The 74 K curves are different in three respects: 1) The early level period persists for a shorter interval. 2) The subsequent drop is much steeper than the 70 K drop. 3) The resistance levels off at a higher value, significantly so for the hydride sample. Note that \(T_a\) for the resistive anomaly in this sample was 72 K. This shows that the annealing
Figure 24. R vs. time for PdH$_{.798}$. This curve was obtained by annealing at 70 K but cooling to 4.2 K for measurements. The two +'s show the points obtained after heating to 90 K and reannealing.
#64  H/Pd = 0.798

$T_A = 80\, K$
Figure 25. Annealing curves for PdD$_{0.75}$ at two annealing temperatures.
D/Pd = 0.75

$T_A = 76^\circ K$

- 70$^\circ K$
- 74$^\circ K$

R (milli-ohms)

$t$ (hours)
Figure 26. Annealing curves for PdH_{0.76}. The R vs. T curve for this sample is shown in Fig. 15.
$H/Pd = 0.762$

$T_A = 72.75^\circ K$

- $70^\circ K$
- $74^\circ K$
Figure 27. Annealing curve for PdH$_{0.78}$. 
H/Pd = 0.78
T_A = 78.25°K
T = 74°K
Figure 28. Resistance vs. time for PdH$_{0.89}$. This sample showed no resistance anomaly as can be seen in Fig. 18.
X-ray #2

H/Pd = 0.89

No Anomaly

$T = 70 \text{K}$

$T$ Stable = 74 K

Increasing
Figure 29. Annealing curve for single crystal PdH$_{.76}$.

At 120 hours in the first run the sample was cooled from 70 K to 65 K.
Single Crystal
D/Pd = .76

- First Run
+ Second Run

T = 70°K
T → 65°K
T = 65°K
can take place even above the anomaly temperature as so defined.

Figures 29, 30, 31, and 32 show the effects of quenching from one annealing temperature to a lower one after $R$ has begun to level off. In each case the cooldown was done as quickly as possible, usually taking a maximum of 15 minutes for the sample to stabilize at the new temperature. Following the quench the resistance again begins to drop sharply and then levels off at a new value lower than the that at the higher temperature.

Figures 33 through 36 show the resistance vs. $T$ curves for some of the samples after annealing. In each case the warming was done very slowly and the samples held at each new temperature several hours before resistance measurements were made. In some cases $R$ was measured at a given $T$ several times over a period of several hours. The curves show a large rise in $R$ from the annealed value. This increase takes place over a broad temperature range. The obvious time dependence of $R$ seen at some $T$'s (for instance at 80 K in Fig. 36) suggests the equilibrium curves may show sharper rises than what is shown here. The discrepancy is not large however. The values measured at some temperatures during warmup are within a few percent of the values the annealing curves were approaching at that temperature. For instance, the 74 K data of Fig. 25 was approaching a limiting value of 2.321 m$\Omega$, compared to the warmup value at 74 K of 2.370 m$\Omega$, a 2% difference.

Each of the $R$ vs. $T$ warmup curves flattens out at some high temperature. For all of the samples shown this breakover temperature is above 80 K. This is much higher than the $T_a$ of the resistance peaks in these samples.
Figure 30. Effect of lowering the annealing temperature on the resistance of PdD$^{.75}$. The 70 K points are the last few points shown on the 70 K curve of Fig. 25.
Effect of Further Cooling on "Annealed" PdD.75 Sample

$\begin{align*}
R & (\text{milli-ohms}) \\
2.40 & \leftarrow 70^\circ\text{K} \\
2.36 & \leftarrow 65^\circ\text{K} \\
2.32 & \leftarrow 60^\circ\text{K} \\
2.28 & \leftarrow 55^\circ\text{K} \\
2.24 & \leftarrow 50^\circ\text{K} \\
2.20 & \leftarrow 45^\circ\text{K} \\
2.16 & \leftarrow 40^\circ\text{K} \\
2.12 & \leftarrow 35^\circ\text{K} \\
2.08 & \leftarrow 30^\circ\text{K} \\
2.04 & \leftarrow 25^\circ\text{K} \\
\end{align*}$

$t (\text{hours}) \rightarrow$
Figure 31. Effect of lowering annealing temperature on PdH. The 70 K data are the last few points of the 70 K data of Fig. 26.
Effect of Further Cooling on "Annealed" PdH.76 Sample

R (milli-ohms)

230 250 270 290 310 330 350 370 390 410 430 450 470

t (hours)→

70°K 65°K 60°K
Figure 32. Effect of lowering annealing temperature on PdH$_{.78}$. The 74 K data are the last few points on Fig. 27.
Effect of Further Cooling on "Annealed" PdH.782 Sample

$T = 74^\circ K$

$T \rightarrow 70^\circ K$

$T = 70^\circ K$
PdD.75
R vs T after annealing

\[ R(\mu) \]

\[ T(\circ K) \]
Figure 35. $R$ vs. $T$ after annealing for $\text{PdH}_{0.76}$. Compare this with the quenched $R$ vs. $T$ curve for this sample shown in Fig. 15.
Figure 36. These data were taken after the first run shown in Fig. 29 was completed.
$R_{\text{vs } T}$ after annealing

$D/\text{Pd} = 0.76$

Single Crystal
C. Discussion

The results of this experiment provide strong evidence that below 80 K some sort of structural phase transformation takes place in Pd-H. If the anomaly were the result of some sort of temperature-induced change in the electronic structure one would expect the resistance change to occur much more rapidly than it does. Given the result that a 40% drop in resistance can take place over a few days, one is forced to think of a change in physical structure.

The form of this phase change is peculiar however. The X-ray and neutron scattering studies cited in Chapter II indicate that this change does not affect the Pd atoms at all. This leaves the possibility that the H atoms are undergoing some sort of order-disorder transition. The earlier searches for an ordered H structure failed, but our results show why that might have happened. The earlier searches held the samples at too low a temperature for too short a time for significant annealing to occur. If one assumes that the drop in resistance begins when the H begins to form a long range order, then the earlier studies would not have shown such an order. This prompted us to undertake a new search for an ordered hydrogen superlattice in a properly annealed sample. This experiment is described in the following chapter.
A. Apparatus

The neutron scattering experiment was performed at the CP-5 Research Reactor at Argonne National Laboratory. The basic parts of the experimental stations are shown in Figure 37. Neutrons from the reactor core were collimated and then filtered by a beryllium single crystal. The arrangement of this crystal and the exit port was such that only neutrons of wavelength .99 angstroms (83.5 meV) were incident on the sample.

The sample was held on the end of a copper probe inside a low temperature cryostat. This cryostat was supported on a series of gimbals which allowed it to be tilted and rotated under computer control. This allowed control of the orientation of the crystal relative to the incident neutron beam, which in effect allowed control of the angle of incidence of the beam on the various atomic planes in the crystal. The detector could be revolved about the cryostat in a horizontal plane to vary the scattering angle being observed.

The entire system was under the control of an IBM 1130 minicomputer. This machine could adjust crystal orientation and detector angle to follow a programmed sequence, and could automatically adjust counting time to compensate for variations in beam intensity. Once the crystal orientation was known the computer could orient the crystal and detector so as to sample the scattered intensity from a given point in the Brillouin zone. Programs existed which allowed automatic determination of crystal orientation and lattice constant, scanning of specified regions of k space, and scanning of specified reflections to determine peak width and integrated intensity.
Figure 37. The neutron scattering experimental station.

Not shown are the temperature control apparatus.
A pressure controller was not available for bath temperature control in this cryostat. We therefore pumped directly on the bath with a mechanical vacuum pump. This lowered the temperature of the nitrogen bath to near 50 K. The sample holder contained both a platinum resistance thermometer and a heater. A feedback temperature controller was then used to control the heater current and maintain the sample T at the desired level.

The sample was a single crystal of Pd 3/8" in diameter by 1.75" long. The sample was cleaned, etched, weighed and then loaded into the high pressure charging apparatus. The crystal was heated in a vacuum to a temperature above the critical point for Pd-D before deuterium gas was admitted. This was done to minimize the lattice damage to the crystal from charging. After the deuterium was admitted and pressurized, the sample temperature was slowly ramped to room T. Immediately after removal from the apparatus, the sample weight was determined and monitored. The weight was seen to slowly decrease with time. When the sample weight reached that corresponding to a D/Pd of .76 the sample was quenched in liquid nitrogen. Subsequently the crystal was held at -78 C for several days to eliminate the uneven distribution of D that would have resulted from the outgassing. The crystal was then low temperature annealed as described in Chapter IV to obtain the R vs. time behavior.

After being loaded into the neutron scattering cryostat the sample was heated to 95 K for 24 hours to erase any previous annealing. The sample was then cooled to 70 K to begin annealing. After one week at 70 K the temperature was lowered to 60 K.
B. Results

Figure 38 shows the Brillouin zone of an FCC lattice like that of Pd-D. The Bragg reflections of the Pd atoms will occur at the center of the zone (the $\Gamma$ point). If the D atoms are completely disordered the Pd reflections will be the only ones observed. This was what we observed at 95 K and is consistent with earlier studies. 27,34,35 The figure shows some of the symmetry directions in $k$ space that were scanned for superlattice lines. Additionally, a series of closely spaced scans were made that had the effect of covering the $k_z = 0$ plane.

As we began this experiment we were aware of several articles dealing with the location of superlattice lines in systems subject to order-disorder transformations. 45-47 Goldberg 48 surveyed this literature, applied it to Pd-D and concluded that superlattice lines were likely to appear at the $X$, $W$, or $L$ points in the zone.

Figures 39 - 42 show the results of some of the scans that were made. As can be seen, no superlattice lines are found at the $X$, $W$, or $L$ points. (The scans $L \rightarrow K$ and $L \rightarrow W$, not shown, were also negative.) Instead, a peak was seen 4/5 of the way from $\Gamma$ to $W$. Several checks were made which showed this was in fact the peak location; it is not a peak at $W$ being erroneously observed. The scan of the $k_z = 0$ plane showed an entire series of such peaks, each 4/5 of the way from a $\Gamma$ point to a neighboring $W$ point. See Figure 43. These lines were not only around the all even FCC reflections; superlattice peaks were also found offset from the (111) Bragg peaks by the same amount.

These intensity peaks are not diffuse scattering peaks but are sharp diffraction lines. This was shown by comparing the full width at half
Figure 38. The FCC Brillouin zone showing the area and directions scanned.
Figure 39. The \( \Gamma \rightarrow X \) scan. The scan was actually done from the \((2\ 0\ 0)\) Bragg peak to the \((1\ 0\ 0)\) location.
Figure 40. The scan \( \Gamma \rightarrow K \rightarrow X \). The scan proceeded from the \((2\ 0\ 0)\) point through the \(K\) point at \((1.25\ .75\ 0)\) to the \((1\ 1\ 0)\ X\) point.
PdD$_{76}$
60°K
$\Gamma \rightarrow K \rightarrow X$

SCATTERED INTENSITY

(580,000)
(200)

$\Gamma$ 0 0.4 0.8 $\xi$

$\xi$ $\xi$ 0

(110)
Figure 41. The $\Gamma \rightarrow L$ scan. The point labeled $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$

is actually the equivalent point $(1.5 .5 .5)$.

The scan began at the $(2 0 0)$ location.
SCATTERED INTENSITY

\[572,000\]

(200)

PdD,76

60°K

\(\Gamma \rightarrow L\)

(1/2, 1/2, 1/2)
Figure 42. The $\Gamma \rightarrow W$ scan. The scan went from the (2 0 0) point to the (1 $\frac{1}{4}$ 0) point. The point marked ($4/5$ 2/$5$ 0) is the equivalent point (1.2 .4 0). Data from two scans done 12 hours apart are shown.
Figure 43. The location of the superlattice lines relative to the Pd peaks. All of satellites shown have been observed. Each of the 0 points is really two reflections, one .2 above the plane shown, and one .2 below the plane.
PdD.76 - 70K
ANNEALING TIME = 1 WEEK

(020) Γ (220)

Γ (000)

Γ

q = (4/5 2/5 0)

■ FCC REFLECTION (h k 0)
□ " " " (1 1 ±1)
• SATELLITE REFLECTION BELONGING TO ■
○ " " " " " " " " " " " □
maximum (FWHM) of the superlattice peaks to that of the Pd Bragg peaks. The FWHM of the (1.2 1.6 0) peak was 1.8° after two weeks of annealing. This compares very favorably with the FWHM of the (0 2 0) peak of 1.7°. This shows that the observed peaks are the result of long range order in the crystal. The intensity of the peaks (see Fig. 42) is very low compared to the Bragg reflections however.

As a first attempt to correlate these superlattice lines with the resistive anomaly we began to warm the crystal from 60 K. Temperature was increased by 5 °K every 12 hours. After each increase the (1.2 1.6 0) peak was repeatedly scanned to obtain the integrated intensity of the peak. Figure 44 shows the results. The intensity I began to drop sharply above 70 K. At 80 K and above the data were noticeably time dependent, with successive scans showing lower I's. The curve made by the last I at each T correlates well with the R vs. T curve of Fig. 36.

The sample was held at 90 K for 3 days and then cooled to 70 K. Figure 45 shows the I vs. time behavior of the (1.2 1.6 0) peak and compares it to the R vs. t behavior. Once again the correlation is quite striking.

C. Discussion

The results of the scattering experiment are clear proof that an ordered superlattice of deuterium atoms does form in Pd-D below 80 K. This superlattice is connected with the results seen in Chapter IV. At present we are unsure of the exact structure of the new phase. We can suggest two different models for the structure:

1) The new structure consists of a deuterium density wave propagating along the [4 2 0] crystal direction. This wave is a periodic variation of the density of D atoms in the (420) planes that lie along the direction
Figure 44. The integrated intensity of the (1.2 1.6 0) superlattice peak during warmup from 60 K to 90 K. For those points that are numbered, between 2.5 and 4 hours at the given T separate each point.
Figure 45. The growth in integrated intensity of the (1.2 1.6 0) peak after cooldown from 90 K to 70 K. The resistance data from the second run shown on Fig. 29 are given for comparison.
Comparison of Resistance and (1.2 1.6 0) Peak Intensity at 70 K
of propagation. The wavelength is 5 of the (420) plane spacings. At present we are unable to specify the phase of the wave relative to the lattice.

If the crystal contained only one such wave it would give rise to only two superlattice lines at (.8 .4 0) and (.8 4 0). The number and location of the peaks we observed indicates that the crystal contains many domains of ordered material. Each domain may have its wave propagating along any of the [4 2 0] directions (there are 12 in all). In effect the deuterium has formed a "polycrystalline" structure although the Pd atoms still form a single crystal. Such a domain structure would give rise to 24 superlattice peaks around every \( \Gamma \) point. Since the ordered material is divided up twelve ways, this would account for the weakness of the superlattice lines relative to those of the Pd peaks.

One objection to this model is that the deuterium does not form a fully ordered structure. Although the D atoms are ordered along the [4 2 0] direction the D atoms in the (420) planes along the wave are still completely disordered. Such a partially disordered structure is not the minimum entropy configuration one would expect at low temperature.

2) The ordered structure may consist of a three-dimensional cubic ordering. The superlattice "unit cell" would have to include several of the Pd unit cells on a side to cause the observed reflections. The 3-D structure that would give rise to the lines we have observed is still unknown. One problem is that we would expect a 3-D structure to give rise to reflections at harmonics of the fundamental reflections, in the same way one sees the (200), (400), etc., peaks in the Pd scattering. A careful search for such extra peaks has been negative.
VI. CONCLUSION

From the data presented in the preceding chapters we draw the following conclusions:

1) A structural phase transformation, involving the H(D) atoms only, takes place below 80 K in Pd-H(D). The exact form of the new structure is unknown.

2) The order parameter for the new phase is temperature dependent. This is shown by the effects of lowering annealing T, and by the breadth of T over which the effects of warmup occur. This in turn suggests that what we see is a second-order phase transition.

3) The time dependencies are due to the low diffusion constant of H(D) in Pd at 70 K. The H(D) atoms are too sluggish to rapidly form the new ordered structure.

4) The formation of the new phase is responsible for the behavior collectively called the "low temperature anomaly." The results of the early experiments stem from the formation of a nonequilibrium, short-range ordered structure. The annealing allows a long-range ordered phase to form, which gives rise to different behavior.

5) The $T_a$ defined in Chapter III and used by other authors is not the temperature of the phase transition. The increase in $T_a$ with H/Pd may indicate nothing more than a decrease in H(D) mobility with increasing concentration.

The preceding results leave several unanswered questions. The three most important are: 1) What is the exact structure of the new phase? 2) What interactions among the atoms in the lattice give rise to this
particular phase? 3) How does the formation of this phase cause the anomalous behavior? These questions will undoubtedly stimulate further studies at low temperature. Our collaborators at Argonne National Laboratory have already begun one such study. Studies on crystals with different D/Pd ratios would also be revealing.

In summary, we have discovered a new ordered phase of deuterium in Pd-D at low temperatures. This new phase is the cause of the low temperature anomaly. We have shown what techniques are necessary to observe this phase. It is to be hoped that this will allow a final solution to this twenty-year-old "minor problem" to be quickly obtained.
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APPENDIX - PHASE DIAGRAM AND STRUCTURE OF PD-H

Figure 46 shows the phase diagram of the palladium hydride system at high temperatures. The alpha phase is a very low concentration phase whose maximum H/Pd ratio is .015 at room temperature. The beta phase is a high concentration phase that covers the H/Pd range from about .6 up to 1.0. The exact minimum H/Pd the beta phase can have (called \( \beta_{\text{min}} \)) is in dispute; Fig. 46 shows an average of the experimental data. Samples containing overall H/Pd ratios between \( \alpha_{\text{max}} \) and \( \beta_{\text{min}} \) consist of microscopic domains of the two phases. Palladium deuteride has a similar phase diagram with a somewhat lower critical temperature (550 K vs. 567 K for the hydride).

The phase diagram at low temperatures is not well known. No studies have been made of the alpha phase solubility at low T. Miller used magnetic susceptibility to find \( \beta_{\text{min}} \) at low temperature for both Pd-H and Pd-D. His results showed \( \beta_{\text{min}} \) to be approximately .63 for both the hydride and deuteride in the range of temperatures in which the anomaly occurs.

Palladium metal has an FCC crystal structure with a room temperature lattice constant of 3.889 Å. When hydrogen is absorbed, the H(D) atoms go into the octahedral interstitial sites in both the alpha and beta phases. At 25°C the alpha phase has a slightly larger lattice constant, 3.895 (3.893) Å for the maximum H(D) solubility. The formation of the beta phase causes a much larger expansion of the lattice. Pd-H(D) at \( \beta_{\text{min}} \) has a room temperature lattice constant of 4.025 (4.027) Å and an \( a_0 \) at 77 K of 4.019 (4.016) Å. Reference 51 showed that the lattice constants of Pd-H(D) increase monotonically with concentration from .63 up to PdH(D)\(_{1.0}\). PdH(D) has the NaCl structure. The Pd atoms still form an FCC lattice, while the H(D)
Figure 46. The high temperature phase diagram of Pd-H.

From Siegel and Libowitz.\textsuperscript{49}
atoms have filled all the octahedral sites to form another FCC lattice that interpenetrates the Pd one. See Figure 47. At lower concentrations some of the H(D) atoms on this lattice are replaced with vacancies. Neutron scattering studies show that at room temperature these vacancies are randomly distributed among the available sites.27,28
Figure 47. The structure of PdH$_{1.0}$. Note both the Pd and H atoms have FCC lattices with the same lattice constant.
- Pd ATOMS
- H ATOMS
VITA

Thomas Edward Ellis was born in Memphis, Tenn. on June 6, 1951. He received his secondary education at John Overton High School in Nashville, Tenn., graduating in 1969. He attended the Massachusetts Institute of Technology for four years, and graduated with simultaneous Bachelor of Science degrees in physics and electrical engineering. Since then he has attended the University of Illinois at Urbana-Champaign, Urbana, Illinois. He was awarded the Master of Science degree in physics in 1974. He is a member of the American Physical Society, the Society of Sigma Xi, and the Phi Kappa Phi Honorary Fraternity.