RAMAN STUDIES OF HYDROGEN VIBRATIONAL
MODES IN PALLADIUM

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RAMAN STUDIES OF HYDROGEN VIBRATIONAL MODES IN PALLADIUM

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The phonon density of states of substoichiometric polycrystalline Pd-H(D) was investigated by Raman scattering above and below the 50 K anomaly. The Raman spectra for hydrogen and deuterium were found to be asymmetric and peaked at 58.5 meV and 39.7 meV, respectively, in near agreement with inelastic neutron scattering data. The scattering mechanism appears to require hydrogen-hydrogen interactions. No major changes in the optical spectra were observed in going through the 50 K anomaly.

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1. INTRODUCTION

With the advent of Raman scattering in solids, a new experimental tool is now in widespread use in measuring the vibrational spectra of solids. The Raman technique has been traditionally used to investigate vibrational modes in molecules and in ionic solids. Within the past ten years, Raman scattering from metallic systems has become possible. Scattering has been used in many ways--from investigating phonon frequencies of simple binary⁽¹⁾ alloys to studying changes in the density of states during phase transformations in layered compounds.⁽²⁾ In the past, inelastic, incoherent, time of flight neutron scattering has been used in measuring the optical phonon density of states in metallic hydride systems.⁽³⁾ But time of flight measurements suffer from poor resolution at high phonon energies and require long count times. Raman scattering has better energy resolution and achieves better count rates due to the experimental method. The present investigation was carried out to see if it is possible to prepare a transition metal hydride sample and to measure its optical vibrational modes.

The palladium hydrogen system was chosen in order to minimize problems caused by surface contamination and because it has been the subject of many experimental and theoretical investigations into its microscopic properties in recent years.⁽⁴⁾ In this thesis, there will be a discussion of the basic ideas of Raman scattering from metals and the experimental setup. The details

of the palladium hydrogen system which are pertinent to this investigation will be discussed, and finally the results of the measurements will be shown which demonstrate that it is possible to measure the density of states of the optic modes of a metal-hydrogen system by Raman scattering.

2. PHASE DIAGRAM OF THE PALLADIUM HYDROGEN SYSTEM

2.1 Phase Diagram

The palladium hydrogen system has been the subject of intense investigation for many years. It is known that palladium is a face-centered cubic structure and hydrogen occupies octahedral interstitial sites⁽⁵⁾ at most concentrations and temperatures. There have been two proposed phase diagrams by Jacobs and Manchester⁽⁶⁾ and they are shown in Figure 1. The main features which are experimentally confirmed are the α and β phases and the existence of the miscibility gap. Both phases are FCC, and hydrogen occupies the octahedral sites. It is believed that the stoichiometric compound, PdH, should be of the NaCl type structure. This is shown in Figure 2.

2.2 The Fifty Degree Anomaly

The most interesting feature of the two phase diagrams occurs at about 50°K where anomalies have been found in many physical quantities for most hydrogen concentrations. The anomaly in specific heat measurements was first reported by Nace and Aston.⁽⁷⁾ The basic shape of the anomaly is shown in Figure 3. Since then, anomalies have been reported in Hall effect, internal friction, electric resistivity, and heat release.⁽⁸⁾ The anomaly occurrence has been observed for many hydrogen concentrations, and its maximum strength occurs at about PdH_{0.63}.

Figure 1. Two proposed phase diagrams of the palladium hydrogen system. The only confirmed features are the α and β phases and the miscibility gap. Taken from Jacobs and Manchester (6).

Figure 2. The proposed structure of stoichiometric PdH with hydrogen occupying octahedral sites.

Figure 3. Temperature dependence of specific heat for $\text{PdH}_{0.63}$ in the 50°K region. Taken from Jacobs and Manchester (8).

This is shown in Figure 4. The amplitude of the anomaly falls in intensity and disappears near $\text{PdH}_{0.90}$ and this leads to the prediction of the γ phase by Jacobs and Manchester. Recently, it has been observed that the anomaly temperature increases at concentrations of hydrogen greater than 0.63 at.% H.⁽⁹⁾ Much research has been done with respect to the anomaly, and many theories have been proposed, but still no firm conclusions about its source can be drawn.

In studying the phenomena associated with the anomaly, neutron diffraction offers a method of studying the structural changes which accompany the phase transformations. The first neutron diffraction experiment was done by Fergusen et al.⁽¹⁰⁾ on samples in the beta phase. It was concluded that a fraction of the hydrogen interstitials moved from octahedral sites to tetrahedral sites upon cooling below the anomaly. The next experiment was done by Entin et al.⁽¹¹⁾ on a sample of $\text{H/Pd} = 0.56$ which is a mixture of the α and β phases. Upon cooling, changes occurred in the diffraction pattern and were interpreted to be a separation of the phases. They concluded that one phase was of low hydrogen content and one of higher content than the original concentration. Further cooling yielded no other changes which support the occupation of octahedral sites by the hydrogen interstitials. This contradicted the results of Fergusen. A third diffraction study was recently reported by Mueller et al.⁽¹²⁾ for concentrations of hydrogen between 0.60 and 0.92 at.% H on single crystals. They found no evidence for a second phase in

Figure 4. Relative magnitude of the anomaly as a function of concentration. Circles are heat release data; triangles and crosses represent resistivity data; and squares are from internal friction experiments. See reference (6).

Amplitude of 50K Anomaly (arbitrary units)

the temperature range of 5 - 300°K. It was again confirmed that the hydrogen atoms occupied octahedral sites.

The anomalies discussed above are consistent with the occurrence of a phase transformation, but the neutron diffraction experiments fail to find evidence of a new phase. This may result from the observation that the time for the transformation is an important factor in experiments related to the anomaly. From observations of specific heat, heat release, internal friction, and resistivity, Jacobs and Manchester⁽¹³⁾ proposed a model in which the anomaly is due to diffusion-controlled martensitic transformation. Their experiments indicated that the transformation would proceed to a limit after each temperature change at a rate which implies the existence of a relaxation time for the transformation. It is proposed that the relaxation time is of the order of one hour at 46°K. This suggests that the reason the neutron diffraction experiments of Mueller and Entin did not observe any phase transition is that they did not allow sufficient annealing times. In suggesting that the anomaly is a diffusion-controlled shear transformation, Jacobs and Manchester expect the motion of the palladium atoms to be the rate controlling factor. In a recent paper,⁽¹⁴⁾ X-ray studies showed that there is no motion of the palladium atoms associated with the anomaly. Now, Manchester proposes that the diffusion-controlled process may be confined to only the hydrogen atoms.

2.3 Hydrogen Ordering Theory

A hydrogen ordering theory has been recently proposed by Satterthwaite et al.⁽¹⁵⁾ By looking at the variations of residual resistivity with time for a sample of $\text{PdH}_{0.8}$ annealed a few degrees below the anomaly temperature, they obtained a curve which is similar to curves obtained from the growth of Gunier-Preston zones in Al-Zn alloys. This resistance behavior of the $\text{PdH}_{0.8}$ alloy suggests that the reordering of hydrogen atoms starts with the formation of 10 - 20 Å zones which coalesce and grow on a time scale of days. The long time constant suggests why previous neutron scattering experiments failed to detect any phase changes.

The ordering is proposed to be due to the electronic structure of the palladium-hydrogen system. The electronic binding predicts the existence of a next nearest neighbor hydrogen-hydrogen attractive interaction.⁽¹⁶⁾ Therefore, ordering will be in such a way as to maximize the occupancy of the next nearest neighbor hydrogen pairs. This would result in ordered phases centered around $\text{PdH}_{0.25}$, $\text{PdH}_{0.50}$, $\text{PdH}_{0.75}$, or PdH . The first two should be unstable due to their location in the miscibility gap. An initial concentration of $\text{PdH}_{0.63}$ would be expected to separate into Pd-H α phase and $\text{PdH}_{0.75}$. Satterthwaite has proposed a neutron diffraction experiment to test this model.⁽¹⁵⁾

3. RAMAN SCATTERING

3.1 Introduction

Raman scattering is the inelastic scattering of photons by matter in which the atomic scattering mechanism (phonons in this investigation) modulates the electronic polarizability associated with each molecule. The theory of Raman scattering is very detailed and is covered excellently in other places.⁽¹⁷⁾ This thesis will only dwell on parts that are relevant in understanding the present experiment.

The process of first order Raman will be discussed initially. The incident photon is characterized by energy $\hbar\omega_L$, wave vector $\vec{k}_L$, and polarization $\hat{e}_L$. The inelastic scattered photons are labelled by $\hbar\omega_s$, $\vec{k}_s$, and $\hat{e}_s$, respectively. In the experiment, the energy difference of the incident and scattered photon is recorded and is related to the energy of the phonon. This is expressed as a conservation of energy in the following:

$$\hbar\omega_L = \hbar\omega_s \pm \hbar\omega_{ph}$$

The plus (minus) sign is for phonon creation (destruction) in a Stokes (Antistokes) process. If the crystal under investigation is free of defects, then the wave number is a good quantum number and

$$\vec{k}_L = \vec{k}_s + \vec{k}_{ph}$$

Wave vectors for the edge of the Brillouin zone are about 10^8 cm^{-1} , while the incident photons have wave vectors at about 10^5 cm^{-1} . The wave vectors for the measured phonons are usually about 10^2 cm^{-1} . Therefore, with respect to the size of the Brillouin zone, the photons are probing phonon energies at the center of the zone in first order Raman scattering.

Processes that involve two phonons are referred to as second order Raman scattering. With the above conservation rules, it is seen that the two phonons must have equal energy and that their wave vectors will be opposite in sign. These phonons can be from anywhere in the Brillouin zone. Therefore, second order Raman scattering can approximate the structure of the density of states.

3.2 Defects and Metallic Scattering

In studying Raman scattering from the palladium hydrogen system, two important features must be considered. First, it is a metallic system, and second, the crystal has up to 37% hydrogen vacancies. Both features can lead to new effects and to experimental problems. The existence of defects destroys the translational symmetry, and wave vector is not conserved in the scattering process. Also defects cause perturbations upon the host lattice phonon spectra and can lead to new modes. The metallic nature of the alloy severely limits the scattering volume by attenuating the signal. There are many review articles⁽¹⁸⁾ which discuss these factors in the literature and the reader is referred to them for the details.

In studying the influence of point defects, the effects of defects are easily classified. The defect, depending upon its coupling to the lattice, will perturb or introduce new vibrational modes. If the frequency of the new mode of vibration is within one of the unperturbed bands, then the mode is referred to as a resonance mode. If the new mode is above the highest band edge or lies between two bands, it is referred to as a local or optical mode. With increasing defect concentration, the local mode can broaden into a band. The most significant effect of defects on the Raman process is referred to as the breaking of the $k = 0$ rule. In the presence of defects, the lack of translational symmetry implies that phonons from anywhere in the Brillouin zone can take place in the scattering process. This implies that the phonon density of states can be measured.

In looking at the scattering of a crystal containing defects, it is best to proceed via writing down the cross section for scattering. The cross section for Raman scattering is

$$\frac{d^2\sigma}{d\Omega d\omega} = K(\omega) \left| \hat{e}_s \cdot \vec{P}_j \cdot \hat{e}_L \right|^2 g(\omega)$$

where $g(\omega)$ is the density of states of the lattice containing defects. $\hat{e}_L$ and $\hat{e}_s$ refer to the polarization of the incident and scattered photon, respectively. The electronic polarizability term enters through its derivative with respect to its configuration coordinate, $(\partial P / \partial X_j)$, where X_j is the basis vector for the irreducible representation of the site group of the

impurity. Through the polarizability term, group theoretical symmetry considerations enter into the cross section.

Stoichiometric PdH has the NaCl structure, and first order Raman scattering is disallowed by symmetry. The introduction of hydrogen vacancies into octahedral sites does not alter this symmetry restriction under the assumption that each hydrogen atom interacts with its nearest neighbor palladium atoms. A nonzero Raman scattering can arise from the hydrogen-hydrogen interactions in the non-stoichiometric alloys. In the presence of hydrogen vacancies the interstitial site symmetry is reduced and no longer is a site of inversion symmetry. Under these conditions the hydrogen interstitial site can be Raman active. The source of these interactions will be discussed later.

The final factor, $K(\omega)$, depends on many things. For defects

$$K(\omega) = \frac{\omega_L \omega_s^3}{c^4} \frac{\hbar}{2\omega} [n(\omega_j) + 1]$$

where ω_L is the incident laser energy, ω_s the scattered photon energy. $n(\omega_j)$ is the phonon occupation number density:

$$n(\omega_j) = (e^{\hbar\omega/k_B T} - 1)^{-1}$$

and $\hbar\omega_{ph}$ is the phonon energy.

In metals, the scattering volume is severely limited. Electromagnetic radiation is heavily attenuated in metallic systems and a skin depth, δ , is introduced to characterize the extent of

penetration:

$$\delta = \frac{\lambda}{2\pi\kappa}$$

λ is the incident wavelength of the radiation and κ is the absorption coefficient. For palladium, an incident photon wavelength of about 5000 Å yields a skin depth of approximately 250 Å.⁽¹⁹⁾ This small skin depth leads to extremely small scattering volumes and requires that the first few hundred angstroms of the sample be typical of the bulk. From the attenuation of the photons in a metal lattice, a δ^5 term enters into $K(\omega)$. This then leads to small count rates.

4. PHONON PROPERTIES OF PdH

4.1 Introduction

In this section, the known lattice dynamics of the palladium hydrogen system will be summarized. Much work has been done on incoherent and coherent neutron scattering with interstitial hydrogen and deuterium. In the first part of this section, we will discuss the microscopic electronic properties of the palladium hydrogen system. It appears that the electronic structure has very important effects on the lattice dynamics of this system.

4.2 Electronic Properties

In the past, the proton model was widely applied to the palladium hydrogen system. In this model,⁽²⁰⁾ the electrons from the hydrogen atoms fill the d band of the transition metal without affecting the shape of the electronic bands. This implies that the hydrogen atoms in the palladium lattice are essentially protons which are screened by the s electrons.

In a series of theoretical and experimental papers,^(16,21) the electronic structure of transition metal hydrides was investigated with an emphasis on the palladium hydrogen system. A conclusion of the study was that the proton model is not totally valid.⁽²¹⁾ It was found that there were low lying states that are a hybridization of atomic palladium and hydrogen states.

The bonding states cause screening effects on the added protons. The effect of each hydrogen atom being screened can lead to hydrogen-hydrogen interactions for the second-like-nearest neighbor hydrogen sites that are attractive. These interactions were predicted by Switendick.⁽¹⁶⁾ Experimental evidence for these interactions and the effects of these interactions on the lattice dynamics was obtained by Rowe et al.⁽²²⁾ and is discussed below.

4.3 Phonon Dispersion Relations

In an extensive investigation of the lattice dynamics of a single crystal of $\text{PdH}_{0.63}$, many interesting features were found. The dispersion relation is shown in Figure 5. First, the acoustic mode frequencies of the deuteride were observed to be 20 - 30% lower than the same modes in pure palladium. This is believed to be consistent with the observed lattice expansion. Also, it is to be noted that other transition metal hydrides undergo the same relative expansion, but their acoustical mode frequencies increase in contrast to palladium. Another observation was that the frequency of the optic mode at the center of the Brillouin zone was low in comparison to other hydrides, implying a weak nearest neighbor Pd-D force constant. The most interesting feature in this experiment was the large amount of dispersion in the optic modes. This dispersion with frequency peak in the L_0 [100] before the zone boundary implies strong second-like neighbor D-D interactions which are comparable to first-like

Figure 5. Phonon dispersion curves for single crystal $\text{PdD}_{0.63}$. Solid curves are calculated via a Born-von Karman fit. Dashed lines are for pure palladium. Solid (open) symbols are for data taken at 150 K (295).

neighbor D-D interactions. These are the hydrogen-hydrogen interactions that were predicted by Switendick. The existence of these interactions is a novel feature of the palladium hydrogen system. These interactions in the nonstoichiometric hydride are believed to be the cause of the modulation of the atomic polarizability that gives rise to Raman scattering.

From the phonon dispersion relationship, it is possible to calculate the phonon density of states. Rowe's calculations for stoichiometric PdD are shown in Figure 6. They neglect the nonstoichiometric nature of the alloy and they further assume that the force constants of the hydride and deuteride are identical. The force constants should not be the same since their data shows strong anharmonic effects. They further believed that only the peak positions, not the shape, would be changed significantly due to the anharmonic forces of the two isotopes. The correctness of the calculated density of state plots is questionable as a result of the neglect of the non-stoichiometric nature of the alloy and the assumption of identical force constants for hydrogen and deuterium.

4.4 Phonon Density of State Measurements

There have been many incoherent time of flight neutron scattering measurements of the density of states of the palladium hydrogen system. Chowdhurry and Ross⁽²³⁾ found that the optic mode peak is at 57 meV with a width of 11 ± 3 meV. This width is over twice the width calculated by Rowe. At first, the

Figure 6. Calculation for the phonon density of states for PdD and PdH from the dispersion relation in Figure 5.

discrepancy was thought to be due to multiphonon effects. Now it is believed that the reason for the large widths is the defect nature of the alloy.

At the recent Hydrogen in Metals Conference, Hunt and Ross⁽²⁴⁾ reported on measurements on the palladium hydrogen system. In Figure 7, the phonon density of states is shown for 70°K. The optic mode is found to be at 58 meV with a broad shoulder on the high energy side. In comparing this data to Rowe's calculation, the isotope dependence of the deuterium and hydrogen optic mode energies is found to be greater than the square root of two, which is expected from the harmonic approximation. Their measured peak was also broader than the one calculated by Rowe, and the explanation comes from a study by Rahman et al.⁽²⁵⁾ which deals with the defect nature of the alloy. This will be discussed later.

A major part of the study by Hunt and Ross dealt with studying the possibility of changes in the phonon density of states at the 50°K anomaly. In Figure 8, the measured density of states for PdD_{0.70} quenched to 10°K is shown with the data for 70°K. There are no significant differences other than a slightly narrower peak at 10°K. This can be due to a decrease of the width of individual phonons and can arise from anharmonic effects. With regard to the annealing behavior suggested by Manchester,⁽¹³⁾ the sample was annealed for several hours below the anomaly temperature and then quenched to 10°K. The comparison of these runs is shown in Figure 9, and no changes are noted.

Figure 7. Data of Hunt and Ross is shown by crosses and circles and is compared to the calculation made by Rowe (22) and to the data of Choudhurry and Ross (23).

Figure 8. The solid line is the measured phonon density of states from Figure 7 and is compared to the run of $\text{PdH}_{0.7}$ quenched to 10 K.

Figure 9. Comparison of measured density of states for a quenched to 10°K run and a sample annealed below the anomaly temperature, then quenched to 10°K.

In view of the recent work by Satterthwaite,⁽¹⁵⁾ these annealing times may not be long enough to cause a significant change in structure. In Satterthwaite's model, an increase in the energy of the optic mode is expected since ordered sites of hydrogen in this model are sites of higher force constants.

The next major study into the lattice dynamics of the palladium-hydrogen system was done by Rahman et al.⁽²⁵⁾ Their study was a combination of experiment and theory in which they found the energy of the optic mode to be 56 meV (Figure 10). The small difference in energy compared to the results of Hurt and Ross is not explicable. The major part of their study was devoted to the investigation of the influence of nonstoichiometry on the lattice dynamics of this system. By using a unit cell, referred to as a "super cell", containing 108 palladium atoms on the face-centered sites and approximately 70 hydrogen atoms randomly located on octahedral sites, they found that nonstoichiometry smears out the spectrum obtained for the stoichiometric hydride. This is shown in Figure 11. They had to increase the force constants derived by Rowe by approximately 20% to obtain agreement with the neutron scattering data for the optic mode position. In harmonic lattices, the effect of isotopes alter the optic mode energy by the ratio of the square root of the masses. A comparison of the optic mode energy found by Rowe and Rahman gives a ratio of 1.5 compared to the harmonic value of 1.414.

Figure 10. Data from experiment by Rahmann et al. (25) compared to density of states calculated by Rowe (22). The tent shape marks on the frequency axis are the uncertainties in the data.

Figure 11. Top curve is density of states calculated by Rowe. Curves A and B are calculated using the supercell to account for the nonstoichiometric nature of the sample. Curve B has force constants 1.2 times the force constants of curve A. The force constants of curve A are those from Rowe.

Glinka et al.⁽²⁶⁾ did a coherent neutron scattering experiment on $\text{PdD}_{0.63}$ to investigate the line shapes of the non-stoichiometric alloys. They also observed an incoherent peak at about 38 meV which is the optic mode energy for deuterium in the palladium lattice.

5. EXPERIMENTAL TECHNIQUES

5.1 Introduction

The typical Raman scattering experiment involves the separation and detection of a very weak signal in the presence of an intense background. Separation of the signal is done by a double monochromator which is analogous to a narrow pass filter. To assist in rejection of stray light, a third monochromator was added in series. The intense background was due to elastic scattering of laser light off of surface imperfections and from imperfections in the monochromator. In the sample used, the worst conditions made detection below 200 cm^{-1} impossible. Added to this is a rising background, believed to be due to sample fluorescence, which can cover up the data.

The experiment required a low temperature environmental stage for Raman scattering, optics, photon counting electronics, and proper sample preparation methods. The photon counting electronics and the low temperature stage are described elsewhere.⁽¹⁷⁾ We will only cover the optical setup and give a brief description of the sample holder and sample preparation.

5.2 Optics

Figure 12 shows a schematic of the optical setup for Raman scattering. Wavelengths used were $5145\text{ \AA}$ (green) and $4880\text{ \AA}$ (blue) at power levels between 400 and 600 mW. The half-wave

Figure 12. Schematic of the optics for Raman scattering.
Insert shows beam's polarization inside and
outside the sample.

plate is for adjusting the polarization of the incident laser beam so that the electric field is in the plane of incidence. The lens focuses the beam onto the sample as a slit of dimensions 2 mm x 25 microns. The angle of incidence is about 70° from the normal of the sample. This reduces the power density while increasing the scattering volume, and, therefore, laser beam heating of the sample is reduced. Following a method used by Holy,⁽¹⁷⁾ the calculated temperature rise is about 10°K for 0.4 watt of laser power at a sample temperature of 50°K and the above slit geometry.

The scattered light is collected through two lenses and enters the Spex 1401 double monochromator. It is then filtered with respect to wavelength and passed into a third monochromator for additional filtering. The photons are detected in a cooled photomultiplier tube and are counted by digital electronics.

5.3 Sample Holder

Samples were cooled in an environmental stage by a continuous flow of helium gas. The system was an Airco Helitran which was modified for continuous flow. Temperatures were measured on a copper block that was in good thermal contact with the sample.

5.4 Sample Preparation

Sample preparation techniques are extremely important for the application of Raman scattering to metallic samples. The choice of the palladium hydrogen system aided in sample

preparation due to the fact that palladium does not oxidize as readily as other transition metals. Samples were 99.9% pure and were in the form of plates of 0.8 mm x 1.6 mm x 0.025 mm. Annealing at 1000°C was carried out at 10^{-6} torr in an oil diffusion pump system using a liquid nitrogen cold trap. Annealing times were about one hour followed by slow furnace cooling.

The next step in sample preparation was to electropolish the surface of the sample. This is a requirement for Raman experiments in metals due to the small scattering volume. Raman requires extremely smooth and shiny surfaces that are characteristic of the bulk. In using mechanical polishing, elastic and plastic strains are introduced, making the surface region uncharacteristic of the bulk. In a study by Brya,⁽²⁷⁾ it was found that mechanically polished samples caused Raman peaks to spread out. Electropolishing palladium leaves a film on the surface of a few angstroms thickness and which is usually transparent at the laser frequencies. The electropolishing solution consisted of one part HCl to five parts acetone. The electropolishing rig was built entirely of teflon with a platinum cathode about a half-inch from the sample. While low electropolishing current densities are typical for many materials, palladium required current densities approaching 2 amps/cm². If the current density is too low, grain boundary etching occurred adding to surface relief which results in increased nonspecular scattering. At high current densities, pitting of the surface starts to occur. The resulting samples tended to have pits and rough surfaces.

The next step in sample preparation was to charge the sample with hydrogen or deuterium. Two possible methods were available: cathodic charging or gaseous charging. Cathodic charging is generally carried out at low current densities and in a dry ice bath using a solution of methanol and HCl.⁽²⁸⁾ This procedure was rejected since as the sample is charged through the miscibility gap (see Figure 1), the nucleation and growth of the β phase will cause surface relief and increase the nonspecular light scattering.

The second procedure is to use gaseous charging techniques. From temperature-composition curves for certain isobars,⁽⁴⁾ it is possible to achieve high concentrations and to avoid the miscibility gap. Heating the sample in vacuum above 300°C and then letting hydrogen or deuterium gas enter followed by proper cooling procedures can achieve concentrations up to $\text{PdH}_{0.80}$ with a pressure of 70 atmospheres. These pressures require a special charging apparatus.

A problem exists at these high concentrations with respect to the leakage of hydrogen from the charged sample. At room temperature and in air, hydrogen diffuses out of the high concentration samples. This problem seems to be most acute for thin samples in that the diffusion of hydrogen can cause the sample to re-enter the miscibility gap. To avoid leakage problems, the samples were placed into liquid nitrogen immediately after charging to reduce the diffusivity of hydrogen. It is important to try to control the concentration of hydrogen since there is evidence

that the energy of the optic mode does change with concentration. Measurements in the α phase by neutron scattering showed an energy of 63 meV,⁽²⁹⁾ while for samples near PdH, superconducting tunneling experiments measured an optic mode energy of 48 meV.⁽³⁰⁾

A final experimental problem was the difficulty in obtaining exact hydrogen concentrations. These were measured using a vacuum extraction technique which determined the hydrogen concentration by volumetric methods. The measured hydrogen concentrations were lower than the values expected to occur with the gaseous charging method. It is not known whether this reflected losses of hydrogen from the specimen during the handling after charging. The specified concentrations will be those from published data.⁽³¹⁾ Another problem in determining hydrogen concentration was that this method gave the average composition of the sample. Light scattering only occurred the first 250 Å of the sample, and the possibility of leakage could have introduced a composition profile and resulted in a lower concentration in the measured volume.

During the many stages of the sample preparation and handling, optical micrography and scanning Auger analysis were used to monitor surface conditions. In Figure 13, the changes in surface relief are shown from an annealed sample in 13(a), then electropolished in 13(b) and 13(c). Figure 14 shows the effect of gaseous charging on surface relief and as seen, there is none. This should be compared to Figure 15, where the micrograph

Figure 13. (a) is a micrograph (160X) of an annealed sample showing grain structure. (b) shows the effect of low current densities during electropolishing; micrograph is at 80X. (c) and (d) are typical of high current densities used in electropolishing. The magnifications were 80X and 320X respectively.

Figure 14. The effect of gaseous charging on surface relief is shown in (a). This is compared to an electro-polished surface in (b). No major differences exist. Magnifications are 160X for both.

a

b

Figure 15. Both micrographs show the effect of the hydrogen being expelled at room temperature in vacuum. -
Micrograph (a) is at 72X and (b) is at 160X.

a

b

shows what happens to surface relief when the hydrogen is expelled in vacuum at room temperature by going through the miscibility gap. This is the same type of relief that is observed by cathodic charging.

The Auger analysis showed that it is possible to prepare a palladium hydride sample and have a "clean" surface suitable for Raman scattering. In the spectra shown in Figure 16, it is seen that in an electropolished sample, the initial surface condition has a strong Pd peak at 330 eV. Other peaks of weaker intensity are sulphur at 151 eV, carbon at 272 eV, and oxygen at 510 eV. A side peak of palladium at 278 eV interferes with the carbon peak. The oxygen peak is weak, indicating that oxidation of the surface is not a problem. Sputtering with argon at 2 kV for one minute removed all major contaminants.

The series of Auger spectra shown in Figure 17 is for a sample that was annealed, electropolished and hydrogen charged using gaseous hydrogen. Contaminant peaks due to sulphur, oxygen and carbon are seen, but they are weak compared to the palladium peak indicating that gaseous charging does not significantly contaminate the surface. Argon sputtering at 2 kV for twenty seconds removed all the peaks except for palladium, indicating a clean surface.

Figure 16. (a) Auger spectrum of an electropolished surface showing a palladium peak at 330 ev. Carbon is at 272 ev and sulphur at 151 ev. Other peaks are side peaks of palladium. Conditions of scan were 2 volts modulation, time constant .1, 5kV accelerating voltage, 40X sensitivity and 1500 for multiplier voltage.

(b) Spectrum is for same sample after one minute of argon sputtering at 2 kV. Same conditions except for 6V modulation, 20X sensitivity and 1350 V for multiplier.

(a)

(b)

Figure 17. (a) Auger spectrum for a charged specimen. Major peaks are Pd 330 ev, 278 ev and sulphur at 151 ev. Conditions are 6V for modulation, .1 sec time constant, 5 kV accelerating voltage, 20X sensitivity and 1300 V on multiplier.

(b) Spectrum after 20 sec Ar sputtering at identical condition except for multiplier voltage is now 1200 V.

6. RESULTS AND DISCUSSION

In this section, the spectra for pure palladium, the palladium-hydrogen system, and palladium-deuteride will be shown. All these spectra were taken in the low temperature stage in a helium atmosphere. Spectra were taken for polarized and depolarized geometry.

The pure palladium spectra taken at about 50°K can be characterized as weak and structureless with a rising background. In a recent spectrum taken by H. Wipf⁽³²⁾ of a single crystal palladium sample in an ultra high vacuum system at room temperature, no structure was seen, and the spectrum was found to be level.

A typical polarized spectrum for palladium charged with hydrogen to $\text{PdH}_{0.79}$ is shown in Figure 18 for temperatures above and below the fifty degree anomaly. In the high temperature spectrum, the optic mode was found to be at 472 cm^{-1} (58.5 meV), in close agreement with the previous neutron scattering experiments. The structure of the peak was found to be asymmetric with a high energy shoulder which agrees with the neutron work. Upon lowering the temperature to 16°K, an identical peak at 472 cm^{-1} was found. The intensity of the peak seemed lowered and this may be related to phonon effects. New structure showed up at 610 cm^{-1} (75.6 meV) in the high energy shoulder. This peak has not been seen before and it may be due to the high energy phonon states away from the zone center. The apparent

Figure 18. Polarized spectrum for $\text{PdH}_{0.79}$. High temperature curve: $T = 51 \text{ K}$, resolution $= 8 \text{ cm}^{-1}$, laser power $= 600 \text{ mW}$, time per point $= 100 \text{ sec.}$, data point interval $= 2 \text{ cm}^{-1}$. High temperature spectrum shifted 30 counts per second up. Low temperature curve has same conditions except for $T = 16^\circ\text{K}$, laser power $= 400 \text{ mW}$ and swell time $= 40 \text{ sec.}$

peak at about 270 cm^{-1} (33.5 meV) may be a two phonon acoustical lattice mode, e.g., the overtone of the 4 THz TA [100] zone boundary mode.

Figure 19 shows the polarized scans for a sample charged to $\text{PdD}_{0.75}$. The optic mode peak was found to be located at about 320 cm^{-1} (39.5 meV), which is comparable to the 38 meV coherent peak found by Glinka et al. The high energy shoulder differs significantly from the hydride. It is not understood what caused the change in the structure. This run was done at 84°K to insure that the sample was above the anomaly temperature. The apparent peak at 630 cm^{-1} (78.1 meV) may be due to a two phonon peak of the optic mode. This high energy peak was not reproducible, thereby casting some doubt on its source. In a search for the overtone in the hydride sample, none was found. Upon lowering the temperature to 16°K , the peak at about 320 cm^{-1} was reproduced. The high energy shoulder still has structure, as can be seen.

Depolarized spectra for both the hydride and the deuteride samples were weak, noisy, and unreliable in their features. They occasionally did reproduce some features of the polarized scans, but with much less intensity. They were sometimes characterized by a rising fluorescent background that covered the features. Figure 20 and Figure 21 show the depolarized spectra for both isotopes.

With respect to the fifty degree anomaly, the results showed that there are no major changes in the density of states

Figure 19. Polarized spectra for PdD_{0.75}. High temperature run is at 84 K, resolution = 8 cm⁻¹, laser power = 400 mW, time per point = 40 sec, data point interval = 4 cm⁻¹. Low temperature curve, same conditions except for T = 18 K.

Figure 20. Depolarized spectra for $\text{PdH}_{0.79}$. Conditions of run, temperature = 55°K , resolution = 8 cm^{-1} , dwell time = 120 sec per point, laser power = 600 mW, data point interval = 2 cm^{-1} . Lower temperature curve has temperature $T = 15^\circ\text{K}$, and same conditions except for laser power = 400 mW and dwell time = 40 seconds per point.

Figure 21. Depolarized spectra for $\text{PdD}_{0.75}$. Conditions were resolution = 8 cm^{-1} , dwell time = 40 seconds per point, data point interval = 4 cm^{-1} and laser power was 400 mW. Top curve has temperature = 78°K and bottom low temperature scan has temperature = 20°K .

upon lowering the temperature below the anomaly temperature. This agreed with the results of Hunt and Ross.⁽²⁴⁾ Long anneals were not tried due to the limitations of the system. In the future, experiments will be done to see if a change in the density of states can be measured according to the ordering theory. An increase in the energy of the optic mode is expected since the ordered sites are sites of higher force constants.

With respect to the isotope shift, a frequency shift of the optic mode of about 1.47 was observed on comparing the results for $\text{PdH}_{0.79}$ and $\text{PdH}_{0.75}$. This should be compared to the value of 1.41 expected from the Einstein harmonic oscillator behavior expected for hydrogen in a palladium host lattice. The larger than ideal isotope effect suggests the presence of anharmonic terms in the lattice potential. These anharmonic forces can arise from the difference in zero point motion of the two isotopes and indicate the possibility of hydrogen-hydrogen attractive interactions.^(23,34)

7. SUMMARY

The study has shown that it is possible to prepare a sub-stoichiometric polycrystalline palladium hydride sample for use in a Raman scattering experiment. This implies that surface contamination is not severe enough to hinder the experiment.

The spectra taken for hydrogen showed the optic mode to be a very broad, asymmetric peak whose maximum was located at 472 cm^{-1} . The width of the peak was measured to be about 70 cm^{-1} , and the shoulder had a width of about 150 cm^{-1} . Upon lowering the temperature to 16°K , the peak position did not change and it was found that a peak at about 610 cm^{-1} developed from the shoulder. The broadness and location of the peak agreed with past neutron scattering experiments. The low temperature peak at 610 cm^{-1} is a new feature in the system.

For the deuteride sample, the peak was found at 320 cm^{-1} with more structure on the high energy side. The isotope shift was calculated to be 1.47 compared to the harmonic approximation value of 1.14. Anharmonic effects were expected to be due to the hydrogen-hydrogen interactions and the large zero point motion of the interstitial. At low temperatures, the deuterium peak was found at 320 cm^{-1} also, with structure on the high energy shoulder.

With respect to the fifty degree anomaly, no changes were found to occur in the peak position of any sample. This lack of

change in the peak position may be attributed to the insufficient annealing times below 50°K.

The observation of Raman spectra from the palladium-hydrogen system, where symmetry disallows the peak, indicates the influence of the hydrogen-hydrogen interactions on the system. It is believed that the interstitial interactions in the hydrogen defect system are responsible for scattering.

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