Title: Measurement of He\textsuperscript{3} Formation in Pd

Author(s): Dale G. Tuggle
           Ricardo B. Schwarz
           Carl J. Maggiore
           Meredith A. Neal
           Mark A. Whitcomb
           Hong T. Bach
           Jyrki E. Vourinen

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Abstract

This is the final report of a one-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). Single crystal palladium samples were both grown at Los Alamos and purchased from a commercial source. These samples were aligned using X-ray diffraction and cut along appropriate crystal planes. After cutting, the samples were mechanically polished and then electro-etched to remove surface damage produced by the cutting and polishing. Ion beam channeling measurements and resonant ultrasound spectroscopy (RUS) measurements were completed on palladium and palladium deuteride samples. The ion beam channeling measurements on palladium samples confirmed the crystal structure and orientation of the samples and the measurements on palladium deuteride samples confirmed the octahedral location of the deuterium atoms in the palladium lattice. RUS measurements of the elastic constants of palladium and palladium deuteride samples were compared to previous measurements. Finally, RUS measurements were also completed on a palladium tritide sample at room temperature.

1. Background and Research Objectives
The goal of this research was to start developing a physics-based understanding of the processes involved in the retention of He in palladium tritide. Empirical studies have shown that helium produced by the decay of tritium is retained in various metal tritide hosts and that this retained helium affects the properties of the host material. It has also been observed that the host material reaches a saturation limit and then starts to release helium. The determination of the parameters that affect this saturation limit is important in predicting the performance of the host material.

2. Importance to LANL’s Science and Technology Base and National R&D Needs
The Laboratory has missions to support the Inertial Confinement Fusion program by developing and loading targets with tritium, to load tritium onto Neutron Tube Targets, and to develop and test tritium production and processing technologies. This research supports primarily the development new tritium processing technologies.

3. Scientific Approach and Accomplishments
The approach taken in this research was to study the early stages of coalescence of atomic helium into bubbles using two techniques: resonant ultrasound spectroscopy (RUS) and ion beam channeling (IBC). RUS is capable of measuring changes in the elastic constants of a single-crystal palladium tritide sample as helium is introduced into the lattice from tritium decays. IBC measurements are capable of measuring the diffusion rate of helium implanted in the surface of a single-crystal palladium deuteride sample. It was expected that measurements using these two techniques would contribute to our understanding of the early stages of helium accumulation in Pd tritide crystals. The hypothesized stages in the retention of helium in a metal hydride lattice are:
(1) Creation of helium atoms in the lattice by the decay of tritium atoms. These helium atoms are hypothesized to occupy octahedral sites in the fcc palladium hydride lattice.

(2) Diffusion of helium atoms and the formation of \( ^3\text{He} - ^3\text{He} \) elastic dipoles due to an attractive force between the helium atoms.

(3) Diffusion of additional helium atoms to the \( ^3\text{He} - ^3\text{He} \) dipoles and formation of aggregates. Calculations suggest that the attractive force between a helium dipole and an additional \( ^3\text{He} \) atom is stronger than the attractive force between two \( ^3\text{He} \) atoms.

(4) Formation of helium bubbles

3.1 Preparation of Pd single crystals and hydrogen charging.

A master single crystal purchased from MaTeck (Julich, Germany) was mounted in a special goniometer that fits both a Laue X-ray diffractometer and a low-pressure diamond-wire saw. The Pd single crystal was oriented in the x-ray diffractometer and then the goniometer was transferred to the wire saw to cut the samples. The master Pd single crystal was cut to produce five oriented single-crystal samples in the shape of parallelepipeds of about 4 x 4 x 6 mm. Two opposite surfaces were oriented normal to the (001) axis of Pd, and the other four had (110)-type indices.

Although the as-cut samples had nearly orthogonal faces, normal to (100) or (110) axes, the orthogonality and alignment of the as-cut samples was not sufficiently accurate for elastic constant measurements using the RUS method. To adjust the orientation, all five samples were therefore polished with 1-\( \mu \)m diamond paste, using a special jig built for this purpose, and using X-ray diffraction measurements.

Palladium sample 9805043B was loaded with hydrogen to form a PdH single crystal. The gas loading was done in a high-pressure furnace built for this purpose. Palladium reacts with hydrogen to form two phases. At low hydrogen concentrations, the hydrogen forms a dilute solid solution, named \( \alpha \). At higher hydrogen concentration, Pd and hydrogen form an ordered cubic \( \beta \) phase. On loading a Pd crystal with hydrogen to form a \( \beta \)-phase single crystal, one must avoid crossing the \( \alpha \)-\( \beta \) coexistence region. Thus, the hydrogen loading was done by first increasing the temperature to 280\(^\circ\)C, then increasing the hydrogen gas pressure to 1000 psi, reducing the temperature (while still under pressure), and finally reducing the pressure. This pressure-temperature path goes over the critical point of the \( \alpha \)-\( \beta \) coexistence range. Sample 9805043A was similarly loaded with deuterium to prepare a Pd-deuteride single crystal.

Figure 1 shows X-ray Laue patterns for sample 9805043B before and after hydrogen charging. The sharpness of the diffraction spots indicates that the deuterided sample is a good single crystal.

3.2 Elastic constants of the five Pd single crystal samples

The three independent elastic constants of all the as-polished samples were measured by the RUS method. Following this initial measurement, the samples were annealed at 1100\(^\circ\)C for 24 hours to remove any damage introduced by the cutting and polishing steps. After annealing, the elastic constants were measured again. The results are summarized in Table 1.
Table 1. Elastic constants of Pd single crystal samples (in units of MPa).

<table>
<thead>
<tr>
<th>Sample</th>
<th>C11</th>
<th>C12</th>
<th>C14</th>
<th>C11</th>
<th>C12</th>
<th>C14</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As-polished</td>
<td></td>
<td></td>
<td>Annealed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9805043A</td>
<td>234.0</td>
<td>179.3</td>
<td>0.723</td>
<td>234.6</td>
<td>182.4</td>
<td>72.35</td>
</tr>
<tr>
<td>9805043B</td>
<td>226.6</td>
<td>176.5</td>
<td>0.708</td>
<td>226.8</td>
<td>176.4</td>
<td>71.91</td>
</tr>
<tr>
<td>9805043C</td>
<td>226.3</td>
<td>176.0</td>
<td>0.705</td>
<td>226.9</td>
<td>176.3</td>
<td>71.38</td>
</tr>
<tr>
<td>9805043D</td>
<td>225.4</td>
<td>175.6</td>
<td>0.691</td>
<td>226.7</td>
<td>176.5</td>
<td>71.01</td>
</tr>
<tr>
<td>9805043E</td>
<td>225.4</td>
<td>175.4</td>
<td>0.696</td>
<td>226.7</td>
<td>176.4</td>
<td>70.76</td>
</tr>
<tr>
<td>Literature</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notice in Table 1 that the annealing caused a slight increase in the elastic constants (between 0.2 and 1 %) due to the elimination of lattice defects such as dislocations and of point defects. Our elastic constant, measured by RUS, are in good agreement with the values reported in the literature [1], which were measured by the pulse-echo method.

3.3 Elastic constants of Pd-deuteride

The elastic constants of the deuterided sample 980543A were measured by the RUS method, and the results are given in Table 2. Our measurements agree well with those of Leisure for PdD0.66.[2] The present work on Pd-deuteride single crystals enabled us to develop the methodology and confidence for measuring the elastic constants of palladium tritides.

Table 2. Elastic constants of single crystal Pd-deuteride (in units of MPa).

<table>
<thead>
<tr>
<th>C11</th>
<th>C12</th>
<th>C14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present work</td>
<td>209.7</td>
<td>157.7</td>
</tr>
<tr>
<td>Literature [2]</td>
<td>210.9</td>
<td>156.5</td>
</tr>
</tbody>
</table>

3.4 Room-temperature elastic constants of a Pd-tritide single crystal

Sample 9805043C was loaded with tritium to prepare a Pd-tritide single crystal. The loading with tritium was done at the Los Alamos WETF tritium facility, following a procedure similar to that developed to prepare a deuterided sample, as described in Section 3.3. The tritium loading was done in a high-pressure furnace [3] located inside a nitrogen-filled glovebox. The elastic constant measurements using the RUS technique were also done inside the glovebox. For this, the pre-amplifier of the RUS equipment was moved inside the glovebox and the electronic signals were transferred to a computer located outside the glovebox via special coaxial cables assembled for this purpose. The measurement of the elastic constants was quite cumbersome because of the difficulty in handling the small single-crystal sample inside the glovebox while using the triple-set of plastic gloves required to protect personnel from the tritium-contaminated atmosphere inside the glovebox.

The RUS measurements as a function of time were taken at room temperature. As expected, the Pd tritide crystal evolved tritium while in the glovebox nitrogen atmosphere. The rate of tritium loss was determined by weighing the sample just before each set of RUS measurements, using a Mettler balance (resolution of 10 µg) located...
inside the glovebox. The tare and sample weights were measured ten times and the averaged difference was used to determine the average tritium content in the Pd-T crystal.

Figure 2 shows the tritium concentration (expressed as the atom ratio of tritium to Pd) as a function of the aging time inside the glovebox. The data shows a clear change in the tritium desorption rate after an aging time of about 60 hr, which we identify as the boundary of the \( \beta \) to \( \alpha + \beta \) phase diagram. The rate of tritium loss is clearly higher in the single \( \beta \) phase and decreases as soon as the sample enters the \( \alpha + \beta \) two-phase region.

Figure 3 shows the \( \beta \)-phase boundary of Pd-T as a function of temperature. Our room-temperature measurement (solid datum, from Fig. 2) agrees well with an extrapolation of the boundary values reported in the literature for measurements at higher temperature. [4]

Figures 4 show the values of C11, C12, and C44 in Pd tritide as a function of tritium concentration. As far as we know, these are the first measurements of the elastic constants of Pd tritide. The three elastic constants change with changing tritium content in the crystal. The straight lines drawn through the data indicate a transition at the same value of T/M =0.618 at which palladium tritide crosses the \( \beta/(\alpha + \beta) \) phase boundary. It is interesting to note that within the \( \beta \) region, C11 and C12 decrease with decreasing tritium content, whereas the shear modulus C44 increases with decreasing tritium content. Within the \( \alpha + \beta \) two-phase region, all three elastic constants decrease with further decrease in the tritium concentration.

The changes in the elastic constants seen in Fig. 4 are due to two factors: (1) the slow loss of tritium, and (2) the incorporation of helium into the palladium-tritide crystal. The first factor has been discussed above. The second factor is discussed next. Tritium decays with a lifetime of about 12.5 years, producing a \( ^3\text{He} \) atom. Because the recoil energy is only on the order of electron volts, each \( ^3\text{He} \) atom remains in the same position previously occupied by the parent tritium atom, namely in a (0,1/2,0) position. Since the \( ^3\text{He} \) atoms have a larger atomic volume than tritium atoms, the \( ^3\text{He} \) atoms create local elastic distortions in the PdT lattice, and this should change the values of the elastic constants. The ultimate aim of this project is to investigate the properties of the \( ^3\text{He} \) distortions by measuring changes in the elastic constants with increasing \( ^3\text{He} \) content in the Pd tritide crystal. This can simply be done by measuring the elastic constants of Pd tritide as a function of time.

The measurements in Fig. 4 were done over the course of one month. During that time, approximately \( \frac{1}{2} \) a percent of the tritium atoms in the Pd tritide crystal decayed into \( ^3\text{He} \). This is a large concentration. It is thus clear that the change in elastic constants seen in Fig. 4 is due both to the partial loss of interstitial tritium and to the partial replacement of \( ^3\text{He} \) for tritium. To separate these two effects we must prevent the loss of tritium in the course of the measurements. This can be accomplished by (a) doing the measurements under an applied pressure of tritium, so as to establish a dynamic equilibrium between the chemical potentials in the gas and in the \( \beta \)-phase tritide, and (b) doing the measurements at cryogenic temperatures, where tritium has negligible mobility. Method (b) is clearly the preferred route since it will further allow us to measure the elastic constants while the \( ^3\text{He} \) atoms are in
their initial interstitial positions, before they have had a chance to diffuse and form 3He-3He dipoles, or larger aggregates.

3.5 Development of a RUS system for measurements in Pd-tritide crystals

We have designed and built a self-contained cryostat system that will enable us to measure the elastic constants of Pd tritide at low temperatures. Operating inside the ESA-TSE gloveboxes, the tritided Pd sample will be positioned in a small stainless steel chamber. This chamber also contains the two piezoelectric transducers needed for the RUS measurements. After sealing this chamber with a compressed copper ring (CONFLAT), the sealed chamber will be removed from the glovebox and will be attached to the cryostat. A vacuum chamber surrounds the sample chamber, and a copper cold finger allows cooling the sample chamber to about 12 K. The whole cryostat system (continuous-cycle refrigerator, sealed vacuum pump, electronic equipment for T measurements, etc) is self-contained in a rolling rack. The temperature of the sample chamber can be continuously controlled between 12 and 300 K.

References
[3] Furnace designed by A. Nobile, ESA-TSE.

Figure Captions:
Fig. 1. Laue X-ray diffraction patterns of the (110) surface of Pd sample 9805043A before (top) and after (bottom) charging with hydrogen into the β phase.
Fig. 2. Desorption of tritium from a Pd single crystal initially in the β tritide phase.
Fig. 3. Temperature dependence of the tritium composition at the boundary between the (α+β) and β phases in Pd tritide.
Fig. 4. Elastic constants of Pd-tritide as a function of tritium content.
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Fig. 2. Desorption of tritium from a Pd single crystal initially in the \( \beta \) tritide phase.

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