論文の内容の要旨

論文題目　Hydrogen quantum diffusion and electronic transport in palladium nanofilms
（パラジウムナノ薄膜における水素の量子拡散と電気伝導特性に関する研究）

氏　　名　小澤　孝拓

Hydrogen, the lightest and smallest element of all atoms, reveals quantum behaviors at low temperature. Quantum tunneling is a typical phenomenon of the nuclear quantum effects, and affected by surroundings of lattice phonons and conduction electrons. On the other hand, hydrogen atoms are readily bonded to various atoms and work as either cation or anion because of its moderate electronegativity. Physical properties of host materials are modulated by hydrogen absorption and adsorption. Furthermore, metastable states and subsurface states potentially have novel electronic and magnetic properties and catalytic reactions. Fundamental understanding of the hydrogen site and interaction with lattice and electrons are essentially important. However, experimental data of hydrogen diffusion at low temperature and its lattice location is lacking due to the difficulty of direct detection of hydrogen atoms by ordinary experimental techniques.

To overcome the difficulty, we focused on the electrical resistance, nuclear reaction and neutron scattering. This doctoral thesis investigated 1) interaction of hydrogen atoms with palladium (Pd) lattice and electrons in hydrogen quantum diffusion, 2) electronic properties in

nm-thick Pd hydrides and 3) structure and dynamics of Pd hydrides. Since Pd is a pure metal and absorbs hydrogen exothermally, Pd hydrides are a good playground to clarify the interaction between hydrogen and Pd atoms. Nm-thick Pd polycrystalline films deposited by magnetron sputtering at room temperature were used. Electrical resistance measurement by a four-terminal method was used to evaluate electronic properties and hydrogen diffusion. We developed a new method, channeling NRA, to analyze the lattice location of hydrogen in crystals. Inelastic neutron scattering was used to investigate the vibrational states of hydrogen atoms in subsurface region.

1) Quantum diffusion of hydrogen in palladium

To detect the hydrogen diffusion, we used electrical resistance measurement. It is a useful way to evaluate the relaxation from metastable to stable states. If the relaxation is caused by hydrogen diffusion, the relaxation time corresponds to the inverse of the hydrogen hopping rate.

Firstly, we focused on the 50 K anomaly, which is a resistance anomaly characteristic of Pd hydrides attributed to ordering of hydrogen atoms in the most stable O sites, and metastable states can be quenched. We observed the resistance relaxation corresponding to the relaxation from the quenched metastable state to the stable state and successfully acquired the relaxation time. Since this relaxation is caused by hydrogen diffusion, the relaxation time of the resistance corresponds to the hopping rate of hydrogen between the O sites. The derived hopping rate showed an upward deviation from the Arrhenius law at low temperature as shown in Figure 1, indicating the nuclear quantum effects. Temperature dependence of the hopping rate and the analysis with WKB approximation revealed that hydrogen diffuses by thermal manner above 100 K and by quantum tunneling below 50 K, and at intermediate temperature region between them the hydrogen diffusion is dominated by quantum tunneling from a thermally excited vibrational state in the O site to the metastable T site. This is attributed to the characteristic potential shape of Pd, where the metastable T site exists between the O sites. On the other hand, the quantum tunneling from excited states was not observed in Pd hydrides with high concentration and Pd deuterides. These results explicitly showed the effect of energy level matching in quantum tunneling. Interestingly, difference of the hopping rates of

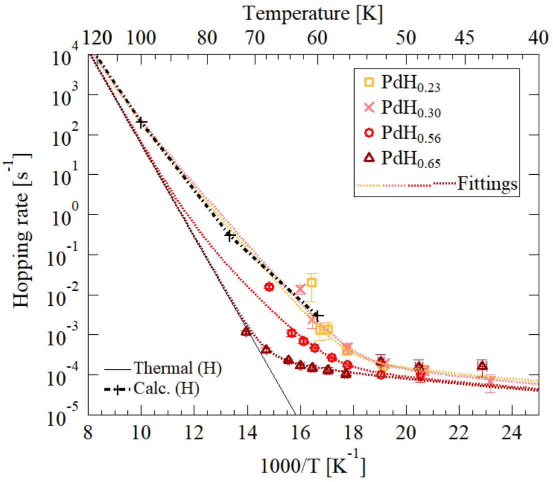

Figure 1. Hydrogen hopping rates in Pd derived by the resistance relaxation associated with 50 K anomaly.

hydrogen and deuterium in quantum tunneling regime below 50 K was smaller than the expectation by the WKB approximation. This implies that the quantum tunneling can be affected by the inter-hydrogen(deuterium) interaction in the collective motion of hydrogen(deuterium) related to the 50 K anomaly.

Secondly, we focused on metastable states of Pd hydrides formed by hydrogen ion implantation. Resistance relaxation was observed after the hydrogen implantation at low temperature. As mentioned in 3), a part of the implanted hydrogen atoms is initially absorbed in the metastable T sites and moves to the O sites by heating up to 100K. Thus, the resistance relaxation corresponds to the hydrogen hopping from T to O sites. The derived hopping rate obeyed the Arrhenius law at high temperature and was almost independent of temperature with a slight increase with decreasing temperature below 20 K as shown in Figure 2. Kondo predicts that the non-adiabatic effect of electrons, where electrons cannot follow the motion of hopping particles and small excitation of electrons are allowed, enhances the quantum tunneling and makes the hopping rate to depend on temperature to a negative power. The present result experimentally verified the theory for the hydrogen tunneling in Pd. From the temperature dependence, particle-electron interaction constant *K* was derived to be 0.41, which is larger than that derived from tunneling of muon in Cu and hydrogen on Cu. We speculate that the large value of *K* in Pd reflects the characteristic band structure of 4d electrons in Pd and/or the asymmetry potential hydrogen passes through from the T to O sites.

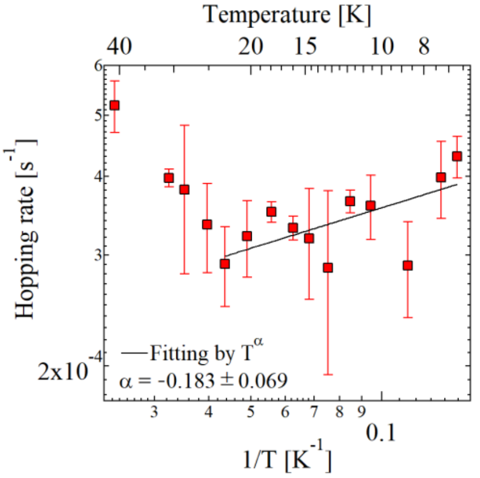

Figure 2. Hydrogen hopping rate in Pd derived by the resistance relaxation after the ion implantation.

2) Resistance minimum in palladium hydrides

We discovered resistance minimum phenomena at low temperature in Pd films. For a 50-nm-thick film, resistance minimum was observed after the hydrogenation as shown in Figure 3. Whereas the 50 K anomaly associated with hydrogen diffusion was suppressed by rapid cooling, the intensity and temperature of the resistance minimum did not depend on cooling rate, implying that this resistance minimum phenomenon is independent of the phase transition by hydrogen diffusion. The temperature of the resistance minimum increased as the hydrogen concentration increased. The temperature and concentration dependence of the resistance minimum temperature were well approximated by a formula of resistance taking into account the Kondo effect. This result demonstrated the possibility for absorbed hydrogen to induce the

Kondo effect in metals. In case of a 5-nm-thick film, the resistance minimum temperature was lower than that of the 50-nm-thick film. This thickness dependence is consistent with previous studies about the Kondo effect in thin films with magnetic impurities. For a 2-nm-thick film, on the other hand, a resistance minimum was observed below 10 K even before the hydrogenation. Since the resistance depends on temperature logarithmically below 10 K, this is attributed to the Anderson localization due to low dimensionality. Hydrogenation of 2-nm-thick Pd brings about another minimum in resistance in addition to the logarithmic feature due to the Kondo effect. The temperature of the resistance minimum is higher than that of the 50-nm-thick film. These results indicated that the Anderson localization and the Kondo effect can coexist and the Kondo effect is enhanced in ultra-thin films due to the surface effects.

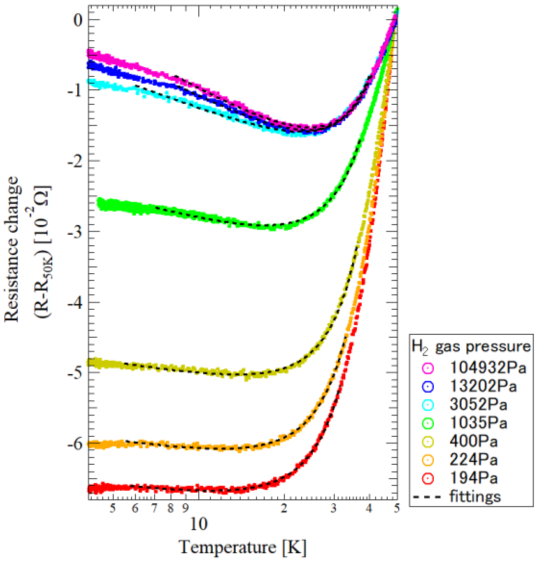

Figure 3. Temperature dependence of the resistance for the 50-nm-thick Pd after the H_2 gas exposure with various pressures at 200 K.

3) Structure and dynamics of Pd hydrides

We developed channeling NRA by combining resonant NRA with $^{1}H(^{15}N, \alpha\gamma)^{12}C$ and ion channeling. This enables us to determine the lattice location of hydrogen in crystals with nm-order depth resolution as well as the hydrogen depth distribution. To realize channeling NRA, we designed and developed the manipulator with a three-axis rotation mechanism capable to precisely control the direction of the sample correctly and arbitrarily. The sample temperature is controlled between 50 and 600 K in an ultra-high vacuum chamber and the in-situ hydrogenation by H_2 gas and hydrogen ion implantation is available. We performed the channeling NRA for Pd(100) hydride formed by hydrogen ion implantation at 50 K, and revealed that a part of the implanted hydrogen atoms are located in the T site at 50 K, and they move to the stable O sites after the 100 K heating.

To investigate the two-dimensional surface effects on vibrational states of hydrogen in Pd, we conducted inelastic neutron scattering experiment for 8-nm-thick Pd hydrides. We successfully obtained the vibration spectrum of hydrogen, and revealed that hydrogen is located only in the O site near the two-dimensional surface similarly to that in bulk. However, the shape of the vibration spectrum is similar to that of nanoparticles. The vibrational state of hydrogen near the surface has both characteristics of bulk and nanoparticle.