Phase boundary study of Pd–H(D) systems by means of electrical resistivity measurements

Hideaki Akaki [a,*], Yuri Sakamaki [a], Shuji Harada [b], Minoru Kubota [c]

[a] *Nagaoka National College of Technology, Nagaoka, Niigata 940-8532, Japan*
[b] *Faculty of Engineering, Niigata University, Niigata 950-2181, Japan*
[c] *Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan*

Abstract

Electrical resistivity measurements were performed on $PdH(D)x$ at high deuterium/hydrogen concentrations in the range $0.916 < x < 0.925$ for $PdDx$ and $x = 0.936$ for $PdHx$. The samples were prepared by electrolysis at low temperatures. Slight differences in the resistivity that were dependent on the rate of cooling, were used to investigate the variation in the phase boundary temperature with hydrogen concentration in the high hydrogen concentration region. The plotted heating curves reveal the dependence of the resistivity on the cooling rates, which we propose originates in a new phase of the system. The temperature of the phase boundary increased with the increase in hydrogen concentration, x.
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1. Introduction

Hydrogen (H/D) atoms in palladium at low temperatures are known to have a large diffusion coefficient due to quantum tunneling [1]. The spaces occupied by hydrogen are reported to be the interstitial octahedral (O) sites of palladium. The number of O sites in the fcc lattice is equal to that of the host atom Pd, so that palladium can absorb large amounts of hydrogen, up to $H(D)/Pd = 1$ [1].

Anomalies of several physical properties, referred to as 55 K anomalies, have been reported for the internal friction [2], electrical resistivity [3–5], and specific heat [6,7] of Pd–H(D) in the low temperature region where the quantum diffusion of hydrogen occurs. It had been thought that these anomalies were caused by an order–disorder transition of hydrogen in Pd. We have reported that the anomaly temperature for the specific heat of the PdHx system increases with an increase in the concentration of hydrogen [7]. Thus, it has been suggested that the phase diagram is not as complex as had been thought in the past, with phase boundaries between some ordered phases [8].

If the anomalous specific heat is caused by an order–disorder transition of hydrogen accompanied by migration of hydrogen, it is interesting to consider the possibility of a phase transition that accompanies the quantum behavior of hydrogen, such as the quantum diffusion of hydrogen.

The electrical resistivity of PdHx and PdDx at high hydrogen concentration in the low temperature region from 130 to 4.2 K has been measured in order to compare the temperature for the anomaly at the phase boundary in PdHx to that for PdDx.

2. Experimental procedure

The sample was Pd (99.95%) with spot-welded lead wires. The loading was carried out at $-70\,^{\circ}C$ with electrolytes of $5.25\,M$ H_2SO_4 in H_2O or $5.25\,M$ D_2SO_4 in D_2O to produce $PdHx$ and $PdDx$, respectively. After loading, the samples were preserved in liquid nitrogen to hinder the loss of hydrogen. For PdHx and PdDx, it has long been known that the superconducting transition temperature increases with increasing concentration of hydrogen [9]. The concentration of hydrogen, x, and the superconducting transition temperature, T_c, are experimentally related by the following expression [9]:

$$T_c = 150.8(x - x_0)^{2.244} \tag{1}$$

where $x_0 = 0.715$ for PdHx, or $x_0 = 0.668$ for PdDx. The concentration of hydrogen in PdHx and PdDx was determined using the above expression and the superconducting transition temperature, T_c, from the measured resistivity. The concentration of hydrogen in PdHx was estimated to be $x = 0.936$ from the super-

* Corresponding author. Tel.: +81 258 34 9428; fax: +81 258 34 9700.
  E-mail address: h-araki@nagaoka-ct.ac.jp (H. Akaki).

conducting transition temperature, $T_c = 5.12$ K. The deuterium concentration for PdDx is estimated as $x = 0.925$, 0.921, 0.918, and 0.916 from $T_c = 7.15$, 6.90, 6.75, and 6.60 K, respectively. The electrical resistivity was determined using the direct current, four-probe method. The influence of the thermal electromotive force was excluded by reversing the current direction. The resistivity measurements were performed during the temperature increase (1 K/min) after quenching or slowly cooling (-1 K/min) from 140 to 4.2 K.

3. Experimental results and discussion

Fig. 1 shows the results measured for Pd, PdHx, and PdDx. Using Matthiessen's rule, the resistivity ρ can be expressed as $\rho = \rho_i + \rho_L(T)$ for temperatures much lower than the Debye temperature, where ρ_i is residual resistivity, and $\rho_L(T)$ is the resistivity that depends on the temperature and is described as $\rho_L(T) = \rho_{ac}(T) + \rho_{op}(T)$, where ρ_{op} is the resistivity caused by optical mode vibration and ρ_{ac} is the resistivity caused by acoustic mode vibration in the hydride. The difference between H and D, according to the difference in the optical vibration mode of hydrogen, is observed in the temperature dependence of the resistivity in the high temperature region.

Fig. 2 shows the dependence of the residual resistance on the concentration of hydrogen. The residual resistivity in the Pd sample was 1.5071×10^{-9} Ω m, due to impurities. From Fig. 2, it seems that the residual resistance of PdDx and of PdHx are in proportion to the hydrogen vacancy concentration $(1 - x)$, and the extrapolated residual resistance value at $x = 1$ becomes almost zero. Therefore, it can be thought that hydrogen vacancies would behave as impurities in PdH$_{1.0}$ or PdD$_{1.0}$.

In Fig. 3, the resistivity after rapid cooling (quenching) is smaller than that after slow cooling below 94 K for PdH$_{0.936}$. Therefore, it is thought that for PdH$_{0.936}$, the slight difference in resistivity occurring at temperature, T_a, is dependent on the cooling rate and exists in the vicinity of 94 K. Similarly, it is thought that for PdDx, T_a exists in the vicinity of 89 K.
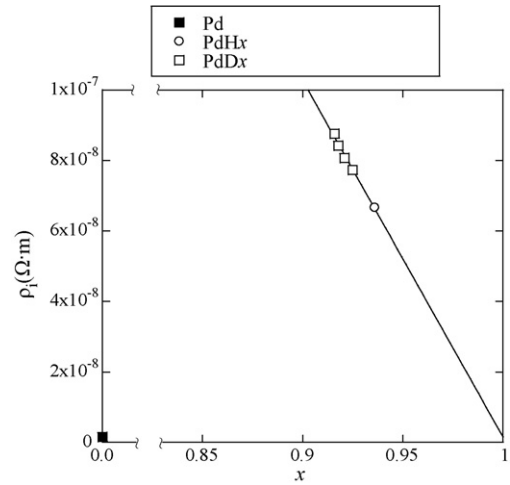

Fig. 2. Dependence of the residual resistivity on the hydrogen concentration, x, for Pd, PdHx and PdDx after fast cooling. The values are in proportion to the hydrogen vacancy concentration $(1 - x)$.
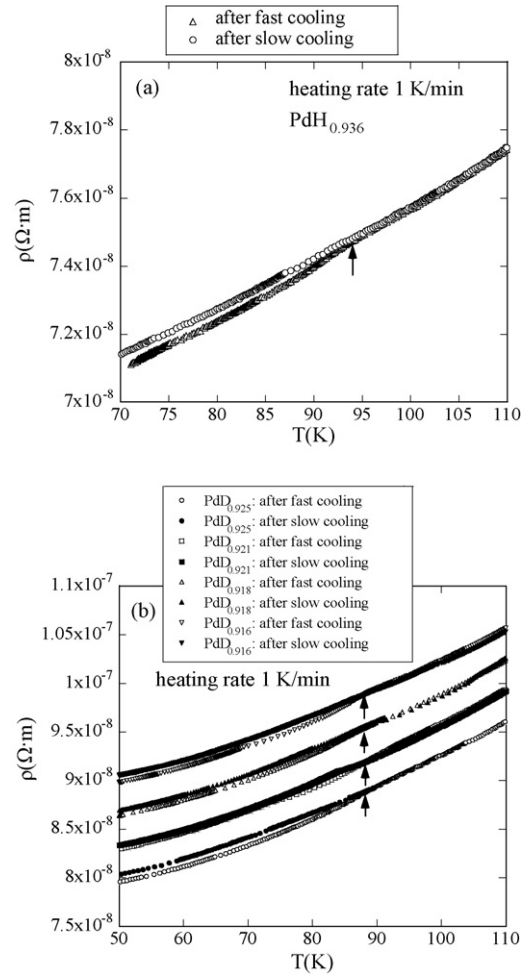

Fig. 3. (a) Dependence of resistivity on the temperature was measured by isochronal temperature increase for PdH$_{0.936}$ after fast cooling (quenching) and slow cooling (-1 K/min). (b) Dependence of resistivity on the temperature was measured for isochronal temperature increase for PdDx after fast cooling (quenching) and slow cooling (-1 K/min). The arrows indicate defined points for the slight differences in resistivity occurring at temperature, T_a.
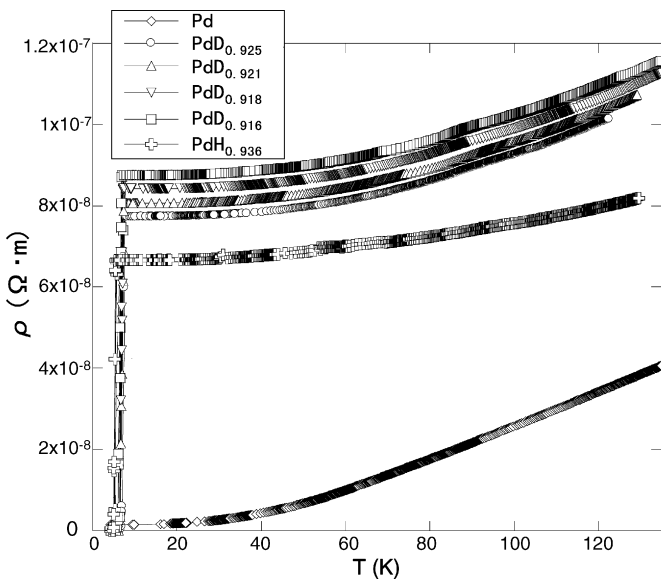

Fig. 1. Isochronal temperature increase resistivity curves for Pd, PdHx and PdDx after quenching from 140 to 4.2 K.
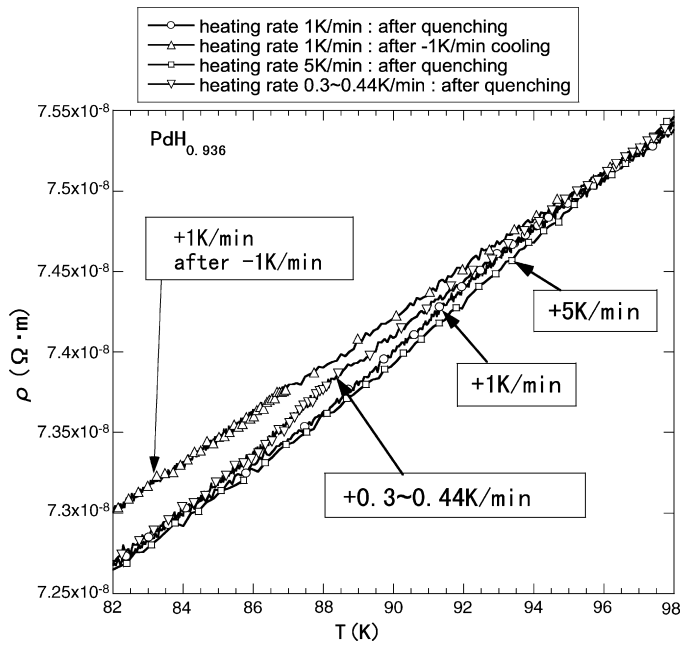
Fig. 4. Dependence of resistivity on the temperature was measured with various temperature increase rates for PdH$_{0.936}$ after fast cooling (quenching) and slow cooling (-1 K/min).
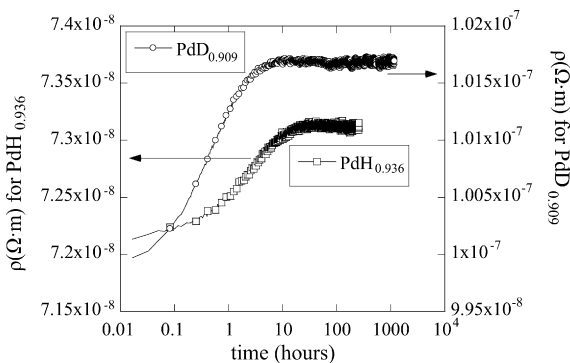

Fig. 5. Dependence of resistivity on the annealing time at 77.4 K for PdH$_{0.936}$ and PdD$_{0.909}$ after quenching from 140 to 77.4 K.

Therefore, it was found that the phase boundary tends toward the high concentration side, compared with the phase boundary temperature rise with increasing hydrogen concentration, as reported from the specific heat anomaly of $x < 0.88$ for PdHx. Some reports do not include evidence for a phase boundary in the high hydrogen concentration region [4,10], because the phase boundary is in a higher temperature region than the respective measurement temperature regions.

Fig. 4 shows the resistivity dependence on the temperature for PdH$_{0.936}$ at different rates of temperature increase. When the sample is annealed (i.e. slow temperature increase) below T_a, it seems that the resistivity increases with the passage of time. Dependence of resistivity on the annealing time is presented in Fig. 5. Previous researchers have reported that the resistivity of Pd–H(D) alloys increases in the early stage of hydrogen ordering, and then decreases in the latter stage of the ordering. This behavior has been explained by nucleation and growth of ordered domains. Until the critical size of the domains is attained, the resistivity increases by the growth of domains, and then the resistivity decreases due to growth above the critical size. The increase in resistivity is caused by an increase in the strained part around the ordered domains. The decrease in resistivity, after the maximum critical size, is caused by a decrease in the strained part due to domain coalescence by growth [5]. However, the resistivity of PdH$_{0.936}$ and PdD$_{0.909}$ only increases at 77.4 K after quenching from 130 to 77.4 K. The decrease in the resistivity by long range ordering or growth of ordered domains could not be observed with annealing at 77.4 K for a period of 100 h. It is not clear whether further annealing is required or whether a different mechanism exists for the anomaly in the region of high hydrogen concentration. Further systematic measurements are required to clarify these issues.

4. Conclusion

A resistivity anomaly was observed for PdH$_{0.936}$ and PdD$_{0.925}$. The temperature at which slight differences in the resistivity occurred, and which were dependent on the cooling rate, were observed at $T_a = 94$ K and 89 K for PdH$_{0.936}$ and PdD$_{0.925}$, respectively. Therefore, the phase boundary tends toward the high hydrogen concentration region. The decrease in resistivity caused by hydrogen ordering was not observed during annealing at 77.4 K for a period of 100 h.

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