

## In-situ Magnetization Measurement of Superconducting Transition in $\text{PdH}_{0.82}$ and $\text{PdD}_{0.79}$ Prepared by Low Temperature Absorption

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We have studied the superconducting properties in palladium (Pd) hydride and deuteride prepared by a low temperature absorption method using in-situ magnetization measurements down to  $T = 0.5$  K. At  $T = 200$  K, the absorption was done under hydrogen ( $\text{H}_2$ ) or deuterium ( $\text{D}_2$ ) gas atmosphere, where the gas pressure and magnetization were monitored simultaneously. From the pressure change caused by the absorption of H (D) in Pd sample, the content was determined to be 0.82 (0.79). The superconducting state was observed below  $T \sim 1.3$  K for the both systems, which was investigated through the precise magnetization measurements. The results suggest that H or D atoms are absorbed uniformly over the whole sample.

Much attention has focused again on superconductivity in hydride systems owing to the recent discovery of superconductivity in sulfur hydride with the transition temperature  $T_c \sim 200$  K.<sup>1)</sup> The first example of superconductivity in hydride was found in thorium hydride ( $\text{Th}_4\text{H}_{15}$ )<sup>2)</sup> in 1970, followed by palladium hydride ( $\text{PdH}_x$  where  $x=\text{H}/\text{Pd}$ ) systems<sup>3)</sup> and Pd-metal-H alloy systems.<sup>4)</sup> These findings triggered a burst of studies on hydrides, revealing many important aspects, especially on the superconducting properties of  $\text{PdH}_x$  systems as follows. 1) The superconducting transition temperature  $T_c$  increases with the hydrogen content  $x$  and reaches at  $T_c \sim 10$  K for stoichiometric PdH.<sup>5,6)</sup> 2) For the same  $x$  content,  $T_c$  in  $\text{PdH}_x$  is much lower than that in the deuteride system  $\text{PdD}_x$ , which is well known as a reverse isotope effect.<sup>5,7,8)</sup> 3) The pressure dependence of  $T_c$  has a negative coefficient.<sup>7,9,10)</sup> 4)  $T_c$  decreases linearly as a function of applied magnetic field  $H$ .<sup>11)</sup> It is worthy to note that the properties for 2) - 4) are clearly inconsistent with the general features of conventional  $s$ -wave superconductors.

On the other hand, such interesting problems in  $\text{PdH}_x$  systems have remained unsolved

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so far because huge interest has been paid to high- $T_c$  cuprate superconductors after their discovery in the latter of 1980's. In addition, a difficulty in the preparation of hydride samples should be pointed out for another reason. The critical content  $x$  for the emergence of superconductivity is higher than  $x \sim 0.7$ , which is not obtained easily as understood from the pressure ( $P$ )-temperature ( $T$ ) phase diagram of  $\text{PdH}_x$ .<sup>12)</sup> Therefore, several methods have been employed to achieve high density state with  $x > 0.7$ . One is use of high pressure environment in which Pd is exposed under a pressurized  $\text{H}_2$  gas. H absorption in the pressure up to  $\sim 3$  GPa was realized using this technique, while a specially designed pressure cell is necessary to accomplish such high pressure.<sup>4,7,10,13–15)</sup> Another is the electrolytic charging method.<sup>5,6,16–18)</sup> This enables easily to obtain a high H content sample without use of high pressure environment, while the in-situ study is difficult. H implantation is a quite powerful method,<sup>19–21)</sup> because the H content does not depend on the equilibrium solubility of the host metal. Hence, this can be applied to many alloys with a low H solubility. For only a narrow region in the specimen, however, H atoms are charged with the same density as far as the constant energy implantation is utilized, meaning that the spatial inhomogeneity of H is inevitable for the sample prepared using this method. Moreover, it is not so easy to determine H content precisely in the latter two cases.

We have studied H absorption process into metals much lower than room temperature using in-situ measurements, demonstrating that the low temperature H absorption method is quite useful to explore the quantum behavior of H in metal-hydrides.<sup>24,25)</sup> According to Akiba *et al.*,  $\text{PdH}_{0.83}$  is prepared even in the  $\text{H}_2$  gas pressure of  $\sim 0.1$  MPa when the H absorption is done at  $T = 210$  K.<sup>28)</sup> This suggests that  $\text{PdH(D)}_x$  with  $x \geq 0.8$  can be prepared at low temperature, enabling to investigate the superconducting properties through in-situ measurements. In this Letter, we propose a new procedure to study the superconductivity of  $\text{PdH(D)}_x$  using a simple setup with a gentle experimental condition, and demonstrate the efficacy of the procedure. After loading H or D with  $x \sim 0.8$  in Pd sample at  $T = 200$  K, we cool down the sample rapidly and perform the in-situ magnetization measurements down to  $T = 0.5$  K. Superconducting transition is clearly seen for the both systems

Pd metal powder with the particle diameter of  $1 \sim 2 \mu\text{m}$  and purity 99.95 % was mounted in a  $^3\text{He}$  insert designed exclusively for a Quantum Design MPMS SQUID magnetometer.<sup>26,27)</sup> After several activation processes by loading and evacuating  $\text{H}_2$  gas at high temperature to remove the surface contamination, the sample space was cooled down to 200K. Next,  $\text{H}_2$  ( $\text{D}_2$ ) gas, which was stored in the reference volume with the initial pressure  $P_{ini}$ , was introduced into the sample space. This leads to a sudden drop for the time evolution of pressure  $P(t)$  due

to the change in the volume space. Note that we must take into account of the decrease of  $P(t)$  caused by the relaxation of the gas temperature because the sample was maintained at 200 K. Such effect was calibrated in a different run. By monitoring  $P(t)$  continuously, H content  $x$  absorbed in Pd was evaluated on the basis of the pressure change of the gas handling system using the Sieverts method.<sup>29)</sup> After finishing the change of  $P(t)$  by reaching the equilibrium state of  $\text{PdH(D)}_x$ , the sample was cooled down to  $T = 25$  K to quench H in Pd. Then,  $\text{H}_2(\text{D}_2)$  gas remained was extracted and  $^3\text{He}$  gas was filled in the insert. Finally, the magnetization measurement was performed down to  $T = 0.5$  K using the MPMS magnetometer with the  $^3\text{He}$  insert.

Figure 1(a) illustrates the time evolution of H content  $x$  and dc magnetic susceptibility  $\chi$  measured under  $H=1000$  Oe at 200 K, which are recorded simultaneously. Pd is well known as a metal close to the ferromagnetic state with a large paramagnetic susceptibility. Indeed, Pd powder used in the present study shows a large value of  $\chi = 5.6 \times 10^{-4}$  emu/mol, which is almost the same to that in previous studies.<sup>30–33)</sup> After introducing  $\text{H}_2$  gas of  $P_{\text{ini}} = 0.185$  MPa in the sample space, the pressure  $P(t)$  decreases gradually as a function of time  $t$ , due to absorption of H into Pd. Concurrently, the magnetic susceptibility decreases rapidly with  $t$  caused by the shift to a paramagnetic state. It becomes zero at around  $t = 2 \times 10^3$  s, where  $x$  amounts to be approximately 0.63 as shown in the inset of Fig. 1. This point corresponds to the boundary concentration  $x_\beta$  in  $\text{PdH}_x$  phase diagram changing from the coexistent  $\alpha + \beta$  to  $\beta$  phases.  $x_\beta = 0.63$  at 200 K is in a good agreement with the value extrapolated from the boundary concentration above  $T = 300$  K.<sup>34)</sup> Note that  $x_\beta = 0.61$  is obtained in our experimental setup at  $T = 300$  K.

After performing further exposure under  $\text{H}_2$  gas,  $x$  reaches the equilibrium value of 0.82 at  $t \sim 10^5$  s ( $\sim$  one day). Then, the sample temperature is cooled down to  $T = 25$  K rapidly. As a result, we expect that the high density state of H with  $x = 0.82$  is kept in the Pd powder.

We measure the magnetization of  $\text{PdH}_{0.82}$  down to  $T = 0.5$  K in the procedure mentioned above. Figure 2 (a) shows the temperature dependence of magnetization  $M(T)$  under several magnetic fields. At  $H = 25$  Oe,  $M(T)$  starts to decrease due to diamagnetization caused by the superconducting transition at around  $T = 1.33$  K, which is assigned as  $T_c$ . By lowering the temperature,  $M(T)$  further decreases and reaches almost a constant value at the lowest temperature 0.5 K. The width of the superconducting transition is less than 1 K, which seems to be sharp enough in comparison with the previous results. With increasing the magnetic field from 25 Oe to 500 Oe,  $T_c$  decreases monotonously. At  $H=1000$  Oe, a slight decreasing is seen in  $M(T)$  below 0.7 K. Judging from the magnitude, this small change should be

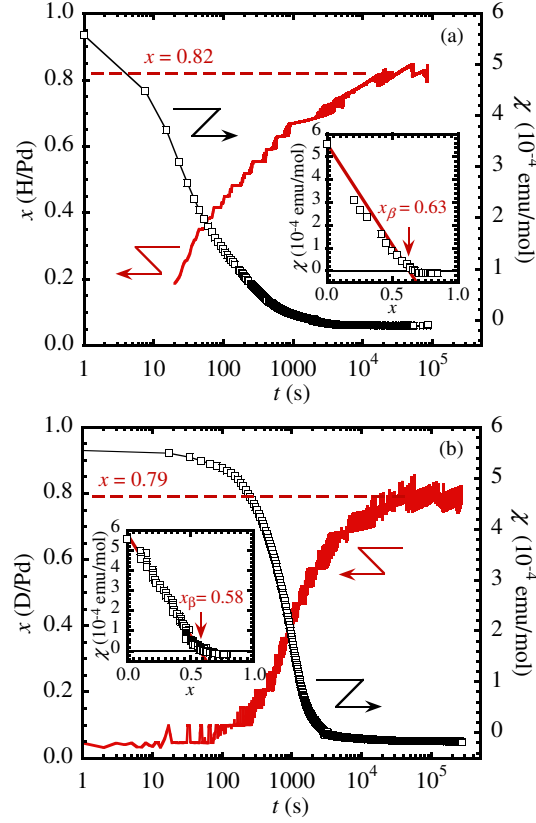


Fig. 1. (Color online) Time evolution of hydrogen content  $x$  and magnetic susceptibility  $\chi$  at 200 K, which are measured simultaneously, for (a)  $\text{PdH}_{0.82}$  and (b)  $\text{PdD}_{0.79}$ . Inset in each figure shows  $x$ - $\chi$  plot.

interpreted by the surface effect of superconductivity as will be mentioned later. We note that the transition temperature  $T_c(H)$  is defined as the intercept point of a linear extrapolation of the magnetization in the superconducting state with the normal-state base line because the point is thought to correspond to the bulk transition temperature. A rounding in the vicinity of the transition is probably caused by a broadening of the transition due to fluctuation of H atom, sample inhomogeneity and surface effects.

At the lowest temperature 0.5 K, the magnetic field dependence of magnetization  $M(H)$  is recorded as shown in Fig. 2 (b). Initially the  $M(H)$  curve decreases steeply up to 75 Oe, and above which it increases gradually to zero magnetization. These behaviors are characteristic to the type II superconductor. The lower and upper critical fields are  $H_{c1} = 75$  Oe and  $H_{c2} = 865$  Oe, which are determined at a peak field and an intersection field with zero magnetization, respectively. Interestingly,  $M(H)$  continues to increase slightly even above  $H_{c2}$  and then merges with an extrinsic linear magnetization at 1525 Oe, which is about 1.7 times as large as  $H_{c2}$ , as indicated in the inset of Fig. 2 (b). Thus this would correspond

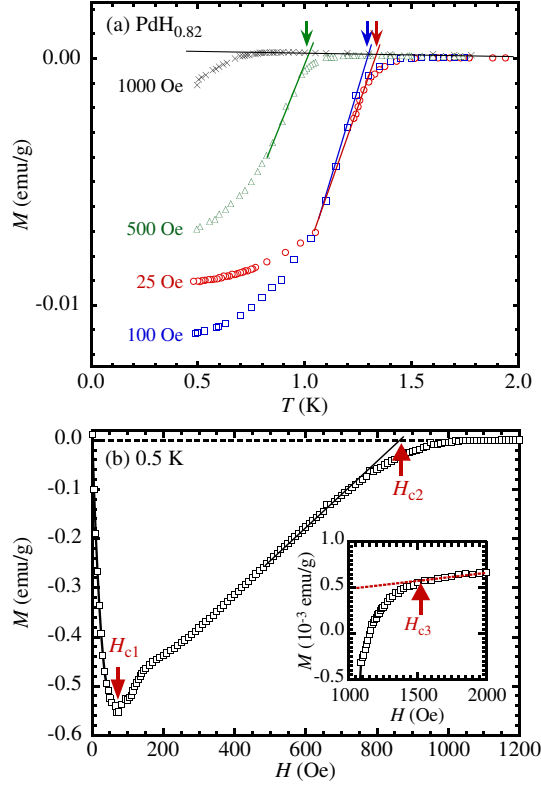


Fig. 2. (Color online) (a)  $M(T)$  under various  $H$  for  $\text{PdH}_{0.82}$ . The magnetic fields are applied at  $T = 10$  K, which is higher than  $T_c$ . (b)  $M(H)$  curve at 0.5 K for  $\text{PdH}_{0.82}$ , measured after zero field cooling. Inset shows enlarged scale version at around  $H_{c3}$

to a surface nucleation field  $H_{c3}$ , where a superconducting sheath subsists in certain surface regions.<sup>35)</sup> High sensitivity measurements by the SQUID magnetometer and a large surface area using the powder sample could enable to detect  $H_{c3}$  in the present study.

Next, we move on to the results for deuteride sample.  $\text{PdD}_{0.79}$  is prepared at 200 K with the same procedure but the initial pressure is increased at  $P_{ini} = 0.327$  MPa. The absorption process and magnetic susceptibility are recorded simultaneously as shown in Fig. 1(b). In spite of the higher  $P_{ini}$ , the reaction is considerably slow and consequently the exposure time to reach the equilibrium state is about  $3 \times 10^5$  s ( $\sim$  three days), which is much longer than that of the H system. These facts suggest that D absorption at  $T = 200$  K is more difficult than H because of the mass difference.<sup>36)</sup> The paramagnetic to diamagnetic switching occurs at around  $x_\beta = 0.58$ , which is smaller than that in the H system and agrees with the reported value.<sup>12,37,38)</sup>

$M(T)$  and  $M(H)$  measured in  $\text{PdD}_{0.79}$  are plotted in Fig. 3 (a) and (b), respectively. The observed features of the superconducting properties in the D system are similar to those in the H system. When the magnetic field is increased,  $T_c$  is suppressed from 1.23 K at 25 Oe to

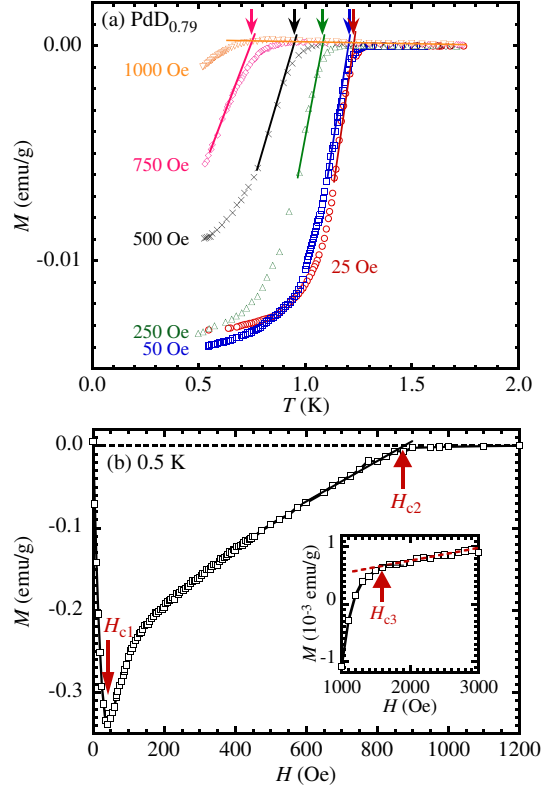


Fig. 3. (Color online) (a)  $M(T)$  under various magnetic fields  $H$  for  $\text{PdD}_{0.79}$ . The magnetic fields are applied at  $T = 10$  K. (b)  $M(H)$  curve at  $T = 0.5$  K for  $\text{PdD}_{0.79}$ , which is cooled in a zero field. Inset is shown for the assignment of  $H_{c3}$ .

0.75 K at 750 Oe as shown in  $M(T)$  curve. From  $M(H)$  curve, the lower, upper critical and surface nucleation fields,  $H_{c1}$ ,  $H_{c2}$  and  $H_{c3}$  at  $T = 0.5$  K are assigned at 40 Oe, 880 Oe and 1590 Oe, respectively.

In order to examine the sample quality prepared by the low temperature absorption, we estimate the superconducting volume fraction  $V_f$ , where  $V_f = -4\pi M_v/H$  and  $M_v$  is the magnetization per volume. To calculate  $V_f$ , we must consider the volume expansion caused by the absorption. In the case of octahedral site occupancy in Pd with fcc structure, H(D)-induced volume expansion  $v_H$  is given by the following relation. Up to  $x = 0.7$ ,  $v_H$  increases linearly with the formula  $2.8x \text{ \AA}^3$  and thereafter bends off with  $0.5(\pm 0.2)x \text{ \AA}^3$  for  $x > 0.7$ .<sup>39–43)</sup> We apply this relation to the both systems because the isotope dependence of the volume expansion is negligibly small between H and D. As a consequence, the volume expansion for  $\text{PdH}_{0.82}$  and  $\text{PdD}_{0.79}$  is estimated to be 11.3 % and 10.8 %, respectively.

We plot the magnetization per volume  $M_v$  for the H and D systems correcting the expansion in Fig. 4. In the estimation, the demagnetizing factor of  $1/3$  is taken into account by

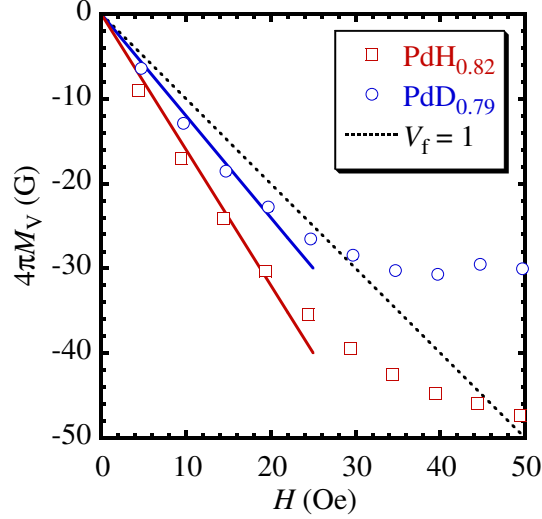


Fig. 4. (Color online)  $4\pi M_v$  as a function of  $H$ . Dotted line indicates perfect diamagnetism with volume fraction  $V_f=1$ .

assuming a spherical shape of powder sample. From a linear slope of  $M_v$  in the initial magnetic field range,  $V_f$ s are estimated to be 1.6 and 1.2 for the both systems, respectively.  $V_f = 1$  in the perfect diamagnetism, so that these values are clearly overestimated. The residual magnetic field in the superconducting magnet is considered as the origin of the overestimation. Additionally, the deviation of the demagnetizing factor due to non-uniformity of the sample powder may give rise to the overestimation. Nevertheless, we believe  $V_f$  is close to unity because the sharp change of  $M(T)$  below  $T_c$  is also understood by assuming  $V_f \sim 1$ . From these facts, we conclude that a high quality sample absorbing H or D atoms uniformly can be obtained by use of the present procedure.

Again, the residual field in the magnet is likely responsible for the difference of  $V_f$  between the H and D systems because  $V_f$  is estimated below  $H = 25$  Oe. Thus the difference of  $V_f$  seems not to be essential. On the other hand,  $H_{c1} = 40$  Oe at  $T = 0.5$  K in  $\text{PdD}_{0.79}$  is nearly a half of  $H_{c1} = 75$  Oe in  $\text{PdH}_{0.82}$ . Such a large shift of  $H_{c1}$  can not be explained only by the residual field. Since the bulk superconducting characters, *e.g.*, the transition temperature and the width of the transition in  $M(T)$  curve, are quite close for the both systems, it is reasonable to consider that the shift is attributable to the difference of the microscopic characters between the two systems. Owing to a non-stoichiometric composition, there remains disorder in H or D atoms occupying at the interstitial sites, which plays an important role for the position of  $H_{c1}$ . As a result of a longer relaxation time as described in Fig. 1, the disorder in the D system should be higher than that in the H system, bringing about a remarkable suppression of  $H_{c1}$ .

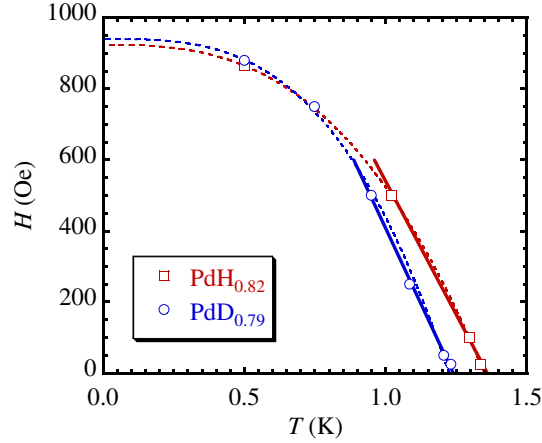


Fig. 5. (Color online) Phase diagram for PdH<sub>0.82</sub> (open squares) and PdD<sub>0.79</sub> (open circles). Dotted curves are least square fittings using a formula described in the text. Initial slopes of phase boundaries at  $T_c(0)$ ,  $(dH_{c2}/dT)_{T_c}$  are indicated by solid lines.

From  $M(T)$  and  $M(H)$  measurements, we obtain the phase diagram shown in Fig. 5, which is consistent with that of conventional superconductors. For PdH<sub>0.82</sub> (PdD<sub>0.79</sub>), the magnetic field dependence of the transition temperature,  $T_c(H)$ , is reproduced approximately by an empirical equation  $T_c(H) = T_c(0)(1 - H/H_{c2})^{1/\alpha}$  with  $\alpha = 2.78$  (3.10) as drawn by the dotted curve in Fig. 5. Note that in high  $H$ -range the  $T_c(H)$  curve deviates from a linear relation reported by Skoskiewicz.<sup>11)</sup> This probably originates from the definition of  $T_c(H)$ , which is determined from the bulk transition in the present study. As discussed above, a tiny diamagnetization is observed in the field region higher than  $T_c(H)$  and  $H_{c2}$ , indicating the survival of superconductivity. If we evaluate  $T_c(H)$  by considering such diamagnetization, the phase diagram is largely modified.

The transition temperature at zero field,  $T_c(0)$ , is estimated to be 1.35 K (1.22 K) by extrapolating the  $T_c(H)$  curve to  $H = 0$ . According to Standley *et al.*,  $T_c(0)$  is given empirically by the relation  $T_c(0) = 150.8(x - x_0)^{2.244}$ , where  $x_0 = 0.715$  and 0.668 for the H and D systems, respectively.<sup>6)</sup> By substituting  $T_c(0) = 1.35$  K (1.22 K) for this relation, the H(D) content  $x$  is expected to be 0.837(0.785), which shows a reasonable agreement with the evaluation based on the pressure change.

Finally we discuss the upper critical field  $H_{c2}$ , which is determined by a combination of two different types of pair-breaking effects, *i.e.* the Pauli paramagnetic and orbital effects. In Fig. 5, the upper critical field at  $T = 0$  K is  $H_{c2}(0) = 923$  Oe (940 Oe), which is much smaller than the Pauli-limiting field, 24800 Oe (22500 Oe), obtained by  $H_p = 1.84 \times 10^4 T_c(0)$ .<sup>44)</sup> This suggests that  $H_{c2}$  is mainly governed by the orbital effect. In the vicinity of  $H = 0$ , the  $T_c(H)$



curves exhibit almost linear temperature dependences, where a Ginzburg-Landau (GL) theory for a type-II superconductor is utilized for the analysis. From the initial slope of  $H_{c2}$  at  $T_c(0)$ , we can estimate the orbital pair-breaking field in the dirty limit using the formula  $H_{c2}^{orb}(0) = -0.69T_c(dH_{c2}/dT)_{T_c}$  shown by Helfand and Werthamer.<sup>45)</sup> In the present case,  $(dH_{c2}/dT)_{T_c} = -1500$  Oe/K ( $-1700$  Oe/K) as indicated by the solid line in Fig. 5, giving  $H_{c2}^{orb}(0) = 1400$  Oe (1430 Oe). Accordingly, the GL coherence length  $\xi(0)$  at  $T = 0$  K can be obtained to be 48.5 nm (48.0 nm) from the relation  $H_{c2}^{orb}(0) = \Phi_0/2\pi\xi^2(0)$ , where  $\Phi_0$  is the flux quantum of  $2.07 \times 10^{-7}$  G/cm<sup>3</sup>. It should be noted that  $H_{c2}^{orb}(0)$  is nearly one and a half times as large as the observed  $H_{c2}(0)$ , indicating the presence of the paramagnetic and spin-orbit effects in the pair breaking.<sup>46)</sup>

In summary, we have studied the superconducting properties in PdH<sub>0.82</sub> and PdD<sub>0.79</sub> prepared by low temperature absorption. After loading H(D) in Pd powder at  $T = 200$  K, we cooled down the sample rapidly and carried out the in-situ magnetization measurements down to  $T = 0.5$  K. The both systems showed superconducting phase transition at around  $T = 1.3$  K. From  $M(T)$  and  $M(H)$  measurements, we estimate the superconducting volume fraction and describe the  $T$ - $H$  phase diagram, implying that H or D atoms are absorbed uniformly over the whole sample. From these results, we conclude that the present experimental procedure combining the low temperature preparation with in-situ measurements provide a new way to reveal the intrinsic nature of superconductivity in PdH(D)<sub>x</sub> system. For the next step, we are planning to prepare the samples with various H and D content by controlling the initial pressure of H<sub>2</sub> and D<sub>2</sub> gas and investigate the concentration dependence through in-situ measurements.

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