STABILITY TEST OF HTSC PHASES IN PdH SYSTEM

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Abstract. In previously published papers, preliminary results on highly hydrogen loaded palladium (PdH\textsubscript{x}) samples with H/Pd stoichiometric ratio x>1, have shown probable multi-phase HTSC superconducting states. In this letter, the stability of the new phases in the sample has been verified. After long-term sample storage of two years at room temperature and room pressure, ac susceptibility measurements in temperature have been done. The sample, that two years earlier exhibited a high temperature phase at T\textsubscript{c}=261.5K with x~1.56, presented now a T\textsubscript{c} shift down to T\textsubscript{c}=160.5K with a x~1.46 and T\textsubscript{c}=82K with a x~1.34. The H/Pd decreases by x~0.1 and ~0.21 while the T\textsubscript{c} diminishes down to T\textsubscript{c}~101K and 180K. In very high x ratio phase, slight hydrogen leakage causes significant T\textsubscript{c} drop. Moreover, another previously existing low temperature phase T\textsubscript{c}=9K with x~1, shifts down to 6K with x~0.85. In this case the decrease of x~0.15 causes the T\textsubscript{c} drop by 3K. In both phases, similar calculated x decrease percentage with subsequent reduction of the T\textsubscript{c} estimated percentage shows a like behavior. This suggests that a single process takes place in the formation of HTSC and low T\textsubscript{c} superconducting state in PdH\textsubscript{x}. The measured PdH sample, before and after long-term storage and trough the thermal cycles, maintains high H loading value with high transition temperatures.

1. Introduction
In the earlier period, PdH system raised great interest for its peculiar properties [1,2]. Palladium is apt to absorb large quantity of hydrogen in the interstitial sites. H is absorbed in octahedral sites in the theoretical stoichiometric ratio x=H/Pd\textsubscript{oct}=1. Moreover there is the possibility for hydrogen to occupy tetrahedral sites in the theoretical stoichiometric ratio of H/Pd\textsubscript{tet}=2 [3,4]. This led to supposition that theoretical maximum stoichiometric ratio is H/Pd=3. Anyhow, there is a great experimental difficulty to achieve stoichiometric ratio H/Pd greater than unit, due to the higher energies involved in filling up of the tetrahedral sites [5]. PdH\textsubscript{x} system shows unusual magnetic properties in function of the H loading: with progressive hydrogen stoichiometry increase at room temperature, the strong paramagnetism of the pure Pd decreases and it becomes diamagnetic at the stoichiometric ratio H/Pd\geq0.7. In pure Pd the 4d shell hybridized with 5s shell contain vacancies. These holes get filled with electrons of the absorbed H atoms and consequent vacancy reduction brings about the diminution and ultimately a quench of paramagnetism. Moreover, PdH\textsubscript{x} with x=0.8 becomes superconductor at the transition temperature T\textsubscript{c~2K}. Proportional relationship between T\textsubscript{c} of PdH\textsubscript{x} and stoichiometry x has been established [6-8]. Recently [9-12], with improved H loading and stabilizing techniques, possible higher superconducting transition temperatures of PdH\textsubscript{x} system have been found. In this
paper, the stability study of the new phases, found in the PdH\textsubscript{x} sample with \(x>1\), has been verified before and after 2 years of sample storage at room temperature and room pressure.

2. Experimental

H is loaded into Pd lattice using an electrochemical cell. The cell geometry consists of two parallel Pt square plates (100x100x0.05mm\textsuperscript{3}) as anodes separated by 15cm of electrolyte. The cathode is a Pd slab sample placed in the middle between the two anodes (4x10x0.05mm\textsuperscript{3}). The electrolyte consists of strontium sulfate (SrSO\textsubscript{4}) dissolved in 18M\(\Omega\)xcm water (10\textsuperscript{-5} M) giving a slightly acid solution (5.0<pH<6.5). The electrolysis requires dc current from 5mA up to 200mA. During electrolysis, to control the H-loading, a four-probe ac resistance measurement of the Pd cathode was taken with a RCL meter at 1mA and 1KHz of sinusoidal current. Highly loaded PdH samples were electrochemically stabilized by adding (10\textsuperscript{-5}M) mercurous sulfate (Hg\textsubscript{2}SO\textsubscript{4}) to the electrolyte. Method details to measure the maximum mean stoichiometric value \(x\) in PdH\textsubscript{x} sample is described in our previous paper [11].

The ac magnetic susceptibility \(\chi'=\chi'_1 + i\chi''_1\) measurements were performed with the liquid helium flow cryostat with enclosed susceptometer. This gradiometer has an in-line double pick-up coil bridge and an exciting external ac magnetic field up to 6G with frequency in the range 31Hz<f<1KHz. The bridge pick-up coil signal, proportional to ac magnetic susceptibility is acquired with a multi-harmonic lock-in amplifier. The sample was cooled down to liquid He temperature in ZFC (Zero Field Cooling) then the temperature was slowly increased up to 300K. Each measurement is a mean value of 5 experimental points while the temperature variation range is 0.01K.

The phase between real \(\chi'_1\) and imaginary \(\chi''_1\) component has been imposed as to minimize the imaginary part at liquid He temperature.

3. Results and discussion

In the previous paper [11], the PdH\textsubscript{x} sample exhibited a probable high temperature superconducting phase, where the real and imaginary first harmonic ac magnetic susceptibility components \(\chi'_1\) and \(\chi''_1\) show the transition temperature \(T_c=263.5K\) and \(T_c=261.5K\). These behaviors are plotted in figures 1A and 1B. The two measurements have been performed with an elapsed time of one week. The critical temperature shift is imputed to a slight hydrogen leakage. In figure 1A the paramagnetic signal due to the measurement apparatus has not been subtracted.

In the same measurement another phase at \(T_c=9K\) was found (Fig. 2). The real component of the ac magnetic susceptibility exhibits the well-known low temperature superconducting phase of PdH\textsubscript{x}.

![Fig.1A - \(\chi'_1\) component of PdH\textsubscript{x} showing HTSC phases. Eq.1 renders \(x_{\text{first}}=1.562\) and \(x_{\text{second}}=1.563\). Elapsed time between the two](image1.png)

![Fig. 1B - \(\chi''_1\) component of PdH\textsubscript{x} showing HTSC phases. Eq.1 renders \(x_{\text{first}}=1.562\) and \(x_{\text{second}}=1.563\). Elapsed time between two](image2.png)
measurements is one week. This phase corresponds to a stoichiometric value $x \approx 1$ \cite{6-8}.

Fig. 2 - $\chi'_1$ and $\chi''_1$ of PdH$_x$ showing low $T_c$ phase. Eq.1 renders $x \approx 1.017$. This low phase was found in same thermal cycle shown in Fig. 1A,1B.

The following equation, described in our previous paper \cite{11} was used for the calculation of stoichiometric ratio $x$ in respect to superconducting transition temperature:

$$x = \left( \frac{T_c}{n} \right)^{\frac{1}{n}} : (n = 7.86) \quad (1)$$

Using this equation, $x$ estimations in superconducting phases shown in fig. 1A and 1B can be done, where $T_c = 263.5K$ and $T_c = 261.5K$ render $x \approx 1.5633 \pm 1 \times 10^{-4}$ and $x \approx 1.5618 \pm 1 \times 10^{-4}$ respectively. Slight hydrogen leakage, $\Delta x \approx 1.5 \times 10^{-3}$, causes significant $T_c$ drop of $\Delta T_c \approx 1.5K$. These HTSC phases with very high $x$ value, exhibit a considerable dependence of the $T_c$ from the H content values.

For the low temperature phase at $T_c = 9K$, found in the same thermal cycle (Fig.1A), with the calculated $x \approx 1.0173 \pm 1 \times 10^{-4}$ the $T_c$ variation is negligible.

Subsequently, the sample has been stored at room temperature and room pressure for two years and then measured. Fig. 3 shows a phase with $T_c = 160.5K$ and a value $x \approx 1.4678 \pm 1 \times 10^{-4}$ has been calculated. In the same thermal cycle, another new HTSC phase, at $T_c = 82.0K$ (Fig. 4), corresponding to $x \approx 1.3476 \pm 1 \times 10^{-4}$ was found. These phases were not present in previous measurements.

High $T_c$ phase with $T_c = 261.5K$ has shifted down to $T_c = 160.5K$ and $T_c = 82K$. For the two new phases the $T_c$ decrease of $\Delta T_c \approx 101K$ (-39%) and $\Delta T_c \approx 180K$ (-67%) correspond to the H leakage of $\Delta x \approx 9.4 \times 10^{-2}$, (-6%) and $\Delta x \approx 0.19$ (-13%) respectively. Moreover, a low temperature phase at $T_c = 6K$ (Fig. 5), with calculated $x \approx 0.9662 \pm 1 \times 10^{-4}$ was found. The low $T_c = 9K$ phase shown in Fig.2, now shifts down to $T_c = 6K$, corresponding to a decrease of $\Delta T_c = 3K$ (-33%) and $\Delta x \approx 5 \times 10^{-2}$ (-5%).

For H loading ratio $x > 1$, the correlation between $\Delta T_c$ and $\Delta x$ confirms the strong dependence of the $T_c$ from x content in PdH$_x$ system. $\Delta x$ de-loading percentage and consequent $\Delta T_c$ decrease percentage are similar in both phases. This leads to supposition that a single process regulates the formation of superconducting states for low $T_c$ as well as for HTSC phases.

Furthermore, the real component $\chi'_1$ in a superconductor is connected with the volume of superconducting phases in the sample \cite{13}. Comparing the $\chi'_1$ behavior of the Fig.2 and Fig.5, it is evident that the magnetic signal and hence the superconducting volume decrease by 10 factor.
The amount of H content in PdHₓ system is associated with the T_c value as well as with the superconducting phase volume.

Fig.4 - χ'_1 of PdHₓ sample showing another new HTSC phase, in the same thermal cycle as in Fig.3. Eq.1 renders x~1.347.

Fig.5 - χ'_1 of PdHₓ sample showing new low T_c phase in the same thermal cycle as in Fig.3. Eq.1 renders x~0.966.

4. Conclusion

Stability of the new HTSC phases in a highly loaded PdHₓ sample with x>1 in time and thermal cycles has been verified. With elapsed time of one week and of 2 years, several HTSC phases in PdHₓ system are still present despite of the slight H de-loading.

Analysis of the new data evidences that absolute variations of T_c with similar Δx in low T_c and HTSC phases in PdHₓ system seem to have dissimilar behavior, whereas the calculated Δx decrease percentage with consequent decrease of the T_c calculated percentage shows an analogous behavior in both phases. This may well imply that in the formation of HTSC and low T_c superconducting states in PdHₓ due to the H-loading, a single process takes place. Moreover, H stoichiometry in PdH sample, affects not only the T_c but also the volume of superconducting domains. Further work on the stabilizing agent technology for x>1 H-loading ratio is in progress as to eliminate even the minute H losses and preserve the HTSC phases nucleated in PdHₓ system.

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