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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_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_c=261.5K with x~1.56, presented now a T_c shift down to T_c=160.5K with a x~1.46 and T_c=82K with a x~1.34. The H/Pd decreases by Δx~0.1 and ~0.21 while the T_c diminishes down to ΔT_c~101K and 180K. In very high x ratio phase, slight hydrogen leakage causes significant T_c drop. Moreover, another previously existing low temperature phase T_c=9K with x~1, shifts down to 6K with x~0.85. In this case the decrease of Δx ~0.15 causes the ΔT_c drop by 3K. In both phases, similar calculated Δx decrease percentage with subsequent reduction of the T_c estimated percentage shows a like behavior. This suggests that a single process takes place in the formation of HTSC and low T_c superconducting state in PdH_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 $x=H/Pd^{oct}=1$. Moreover there is the possibility for hydrogen to occupy tetrahedral sites in the theoretical stoichiometric ratio of $H/Pd^{tet}=2$ [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_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≥0.7. 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_x with x=0.8 becomes superconductor at the transition temperature T_c~2K. Proportional relationship between T_c of PdH_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_x system have been found. In this paper, the stability study of the new phases, found in the PdH_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 ($100x100x0.05mm^3$) as anodes separated by 15cm of electrolyte. The cathode is a Pd slab sample placed in the middle between the two anodes ($4x10x0.05mm^3$). The electrolyte consists of strontium sulfate ($SrSO_4$) dissolved in 18MΩxcm water (10^{-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^{-5}M) mercurous sulfate (Hg_2SO_4) to the electrolyte. Method details to measure the maximum mean stoichiometric value x in PdH_x sample is described in our previous paper [11].

The ac magnetic susceptibility $\chi_1 = \chi'_1 + i\,\chi''_1$ 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 χ'_1 and imaginary χ''_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_x sample exhibited a probable high temperature superconducting phase, where the real and imaginary first harmonic ac magnetic susceptibility components χ'_1 and χ''_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_x

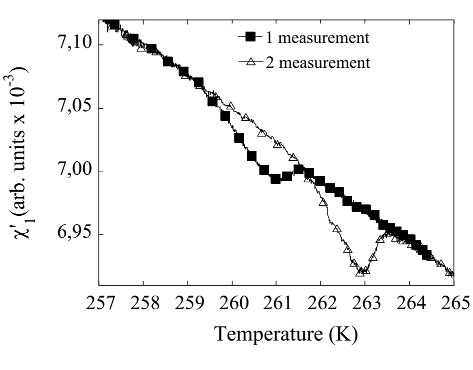

Fig.1A - χ'_1 component of PdH_x showing HTSC phases. Eq .1 renders x^{first}~1.562 and x^{second}~1.563. Elapsed time between the two

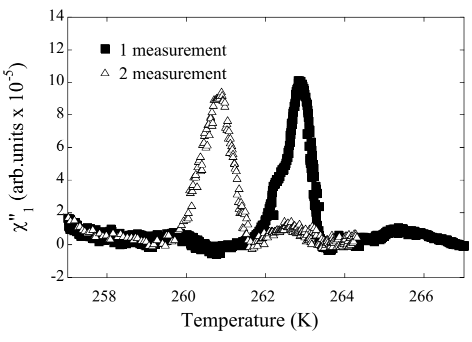

Fig. 1B - χ''_1 component of PdH_x showing HTSC phases. Eq.1 renders x^{first}~1.562 and x^{second}~1.563. Elapsed time between two

measurements is one week. measurements is one week.
system [6-8]. This phase corresponds to a stoichiometric value x~1 [6-8].

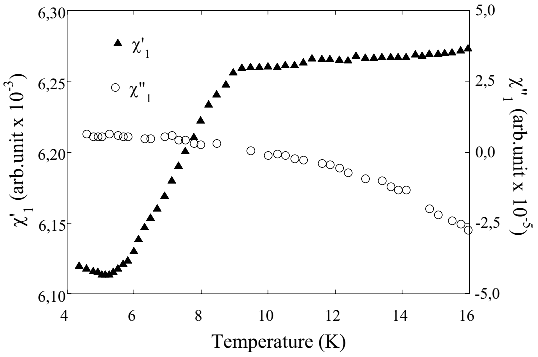

Fig. 2 - χ'_1 and χ''_1 of PdH_x showing low T_c phase. Eq.1 renders x~1.017. This low phase was found in same thermal cycle shown in Fig. 1A,1B.

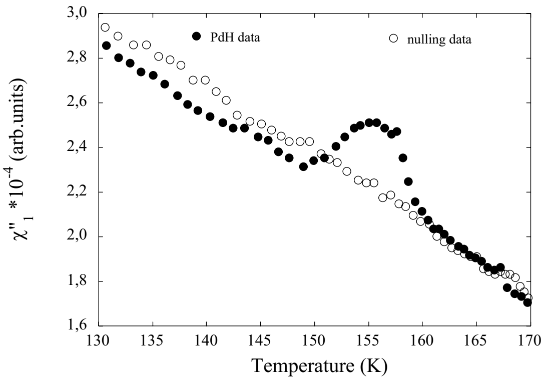

Fig. 3 - χ''_1 of PdH_x showing a new HTSC phase. Eq.1 renders x~1.468. Test performed on the same sample two years after the measurements shown in Fig.1A,1B, and 2.

The following equation, described in our previous paper [11] was used for the calculation of stoichiometric ratio x in respect to superconducting transition temperature:

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

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~1.5633±1x10^{-4} and x~1.5618±1x10^{-4} respectively. Slight hydrogen leakage, Δx~1.5x10^{-3}, causes significant T_c drop of ΔT_c~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~1.0173±1x10^{-4} the T_c variation is neglectable.

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~1.4678±1x10^{-4} has been calculated. In the same thermal cycle, another new HTSC phase, at T_c=82.0K (Fig. 4), corresponding to x~1.3476±1x10^{-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 ΔT_c~101K(-39%) and ΔT_c~180K (–67%) correspond to the H leakage of Δx~9.4x10^{-2}, (-6%) and Δx~0.19 (-13%) respectively. Moreover, a low temperature phase at T_c=6K (Fig. 5), with calculated x~0.9662±1x10^{-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 ΔT_c=3K (-33%) and Δx~5x10^{-2} (-5%).

For H loading ratio x>1, the correlation between ΔT_c and Δx confirms the strong dependence of the T_c from x content in PdH_x system. Δx de-loading percentage and consequent ΔT_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 χ'_1 in a superconductor is connected with the volume of superconducting phases in the sample [13]. Comparing the χ'_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 PdH_x system is associated with the T_c value as well as with the superconducting phase volume.

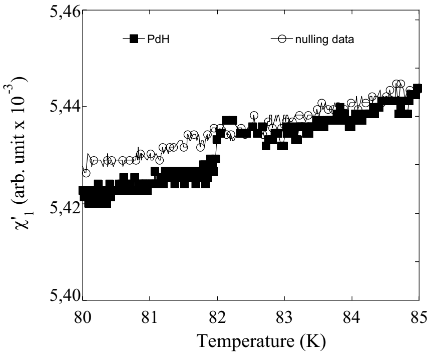

Fig.4 - χ'_1 of PdH_x sample showing another new HTSC phase, in the same thermal cycle as in Fig.3. Eq.1 renders x~1.347.

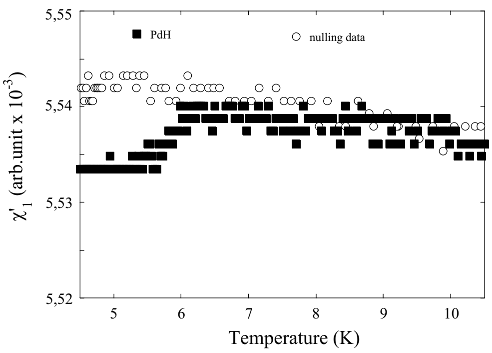

Fig.5 - χ'_1 of PdH_x sample showing new low T_c phase in the same thermal cycle as in Fig.3. Eq.1 renders x~0.966.

4. Conclusion

Stability of the new HTSC phases in a highly loaded PdH_x 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 PdH_x 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 PdH_x 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 PdH_x 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 PdH_x system.

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