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A REVIEW OF HIGH TEMPERATURE SUPERCONDUCTING PROPERTY OF PDH SYSTEM

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The discovery of superconductivity in palladium-hydrogen (PdH) and its isotopes (D,T) at low temperature, brought about extensive study of this system. These studies have shown that the critical transition temperature is a function of the H concentration x in the PdH_x system with T_c=9K for x=1. In the last decade we defined a room temperature and room pressure technique to load H and maintain stable the stoichiometry in Pd lattice at levels higher than unit. Several magnetic and electric transport measurements have been performed showing transition temperature in the range of [18K< T_c < 273K]. Moreover in a typical critical current measurement configuration, current density greater than $6*10^4$ Acm^{-2} has been measured at liquid nitrogen temperature. The 263.5K superconducting transition after a week of sample storage at room pressure and temperature, decreased down to 261.5K and after 2 years it became 160.5K, demonstrating a fairly good stability of the sample. Evidences of the flux exclusion (ZFC measurements) and the flux expulsion (FC measurements) have been found at very high transition temperature (Tc=235K) for the PdH system.

Keywords: Palladium-Hydrogen; superconductivity; Meissner effect.

1. Introduction

Since the beginning of the last century, of all metal-H systems, the Palladium-Hydrogen has been the most extensively investigated (PdH_x, where x=H/Pd ratio). In Pd the 10 electrons of d-band $4d^{10}$ are shared between two zones: E_F intersects the 4d and the broad 5sp bands [1, 2]. There are 0.36 electrons in the 5sp band and equal number of positive holes of unfilled state in the d shell. Pd absorbs H very easily and in large amount, because the electron of the H goes into the d shell, thereby the number of positive holes decreases and E_F value does not increase. The PdH_x magnetic susceptibility χ, in function of stoichiometry x, at 300K decreases with the x increase, passing from a strong paramagnetic behavior of pure Pd, 550-600x10$^{\text{\textbackslash}6}$ cm^3/moles, to a clear diamagnetic behavior [3]. The studies of low temperature anomaly correlated with the high stoichiometric value x ($0.75 \leq x \leq 1.0$) of PdH, led the experimenters to the discovery of superconductivity in PdH [4], and the T_c dependence on stoichiometry x ($1.5 \leq T_c \leq 9.0$) [5]. In this context, many experimental results on probable HTSC in PdH_x have been described in previous papers [6, 7, 8, 9] after that the sample preparation method, to assure stable and high stoichiometry x>1 in PdH, has been defined.

2. Superconductivity Measurements

An important measurement of the superconductivity is the critical current. The I-V characteristic of a PdH_x sample at LN_2 temperature shows superconducting critical current greater than J_c>6§10^4 Acm^{-2} (Figure 1). The I-V value threshold is by 2 orders of magnitude higher, as we have already underlined in the reference [6]. However, our evaluation is based on the fact that the voltage drop on the PdH_x wire at 77K is a constant value with a variable current I. This cannot be a behavior of a normal resistance since there is no slope of the I-V characteristic. Moreover, the rapid increase of the voltage drop V around the current value of 1A shows a swift resistance raise, indicating a possible critical current value of the sample with x>1 at 77K.

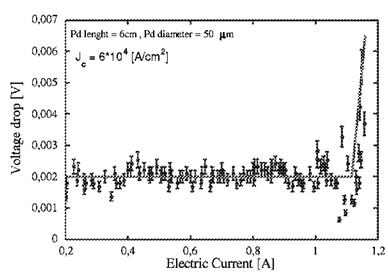

Fig. 1. Characteristic V-I for a PdH wire 50μm in diameter and 6 cm long at 77K.

In order to measure the ac magnetic susceptibility, slab samples (20x4x0.05mm^3) have been prepared and stabilized [8]. The first thermal cycle evidenced a potential SC transition phase with a significant signal of the imaginary component χ''_1 at T_c=263.5K (blue line in figure 2) and another phase at lower temperature T_c=235K (figure 3) both related to PdH_x zones with stoichiometry x>1. A week later, the same measurement procedures were repeated on the sample (red line in figure 2), and the critical temperature of new phase shifted down to lower temperature T_c=261.5K (slight deloading, probably due to thermal cycles), while the phase at 235K remains unvaried. Subsequently, to monitor the stability of this new probable HTSC phases in a highly loaded PdH_x sample with x>1 in time and thermal cycles, this sample has been stored at room temperature and room pressure for two years and then measured again [9]. Green line in figure 2 shows the shift of the 261.5K transition phase to lower temperature T_c=250.5K. This phase was not present in previous measurements.

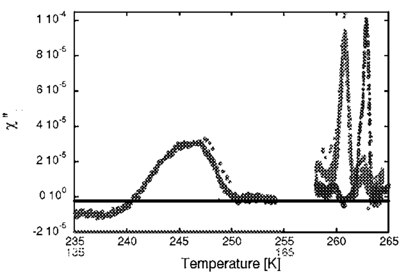

Fig. 2. Imaginary component of the ac magnetic susceptibility of PdH sample, showing the shift in temperature due to the slight hydrogen loss.

Comparison of the transitions at 261.5K and 260.5K, evidences that the signal amplitude decreased by factor 3 and the temperature transition width increased by factor 5, while another phase, of the same sample shows a very good stability T_c=235K in all measurement cycles (red line in figure 4).

There are two aspects regarding the perfect diamagnetism of the superconductors: the flux exclusion underlined by the ZFC measurements and the flux expulsion (Meissner effect) underlined by FC measurements. In superconducting materials with strong pinning (important for the critical current amplitude) the FC signal is lower than the ZFC. This because the pinning prevents the vortices motion and the presence of internal magnetic fluxon field in the sample decreases the superconducting diamagnetic signal [10]. The comparison between ZFC (Zero Field Cooling) and FC (Field Cooling) signals of the first harmonic component for this 235K transition is shown in figure 4.

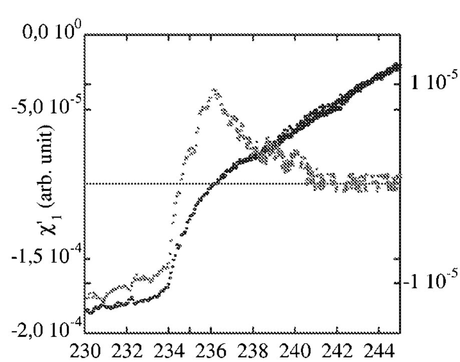

Fig. 3. Real and Imaginary component of PdH_x sample at T_c=235K.

The sample is cooled down in ZFC to 190K, the phase is set to zero at T=200K and then measured. The same procedure has been used, cooling down the sample with 6G of ac magnetic field with the same phase setting versus temperature. The ZFC amplitude is higher than the amplitude of the same sample signal measured in FC which sustains the superconducting aspect of this $PdH_{x>1}$ phase.

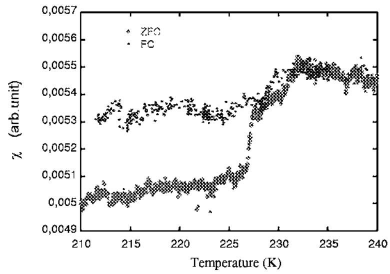

Fig. 4. FC, ZFC measurement of ac first harmonic real component of PdH_x phase at 235K.

A final consideration goes to the stoichiometric value x achieved in our samples. The laminar sample shown in this paper has been prepared for magnetic measurements in the gradiometer. The effective stoichiometry x as an in-line experimental datum has not been measured. On the other hand, we have extensively studied the stoichiometry in PdH samples using the 'resistance' method described in reference [8], based on R/R_0 ratio value correlated with x value, where R_0 is the initial pure Pd resistance and R is the PdH_x resistance for specific x value. This method, due to the sensitivity of the resistive measurement, renders significantly precise mean value: $x \sim 1.45 \pm 0.01$.

According to our phenomenological model, for this stoichiometric value a superconducting transition around T_c=146K would be expected if hydrogen was homogeneously loaded in the sample. This was not observed but a wide transition temperatures range has been found, probably due to the non-homogeneous H loading areas inside the sample.

3. Conclusion

To complete our previously presented measurements on probable HTSC property of $PdH_{x>1}$, the expulsion of magnetic field (Meissner effect) has been compared with the exclusion of magnetic field in PdH_x sample. The lack of substantial Meissner signal might be explainable by substantial vortex pinning.

Acknowledgments

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