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Magnetic and transport properties of PdH: intriguing superconductive observations

Magnetic and Transport Properties of PdH: Intriguing Superconductive Observations*

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Since the discovery of superconductivity in palladium-hydrogen (PdH) and its isotopes (D,T) at low temperature, several efforts have been made to study the properties of this system. Superconductivity of PdH system has been initially claimed by resistance drop versus temperature and then confirmed by dc magnetic susceptibility measurements. These studies have shown that the critical transition temperature is a function of the hydrogen concentration x in the PdH_x system. In all these experiments, the highest concentration x of hydrogen in palladium was lower than the unit. In the last decade we defined a room temperature and room pressure technique to load hydrogen and its isotopes into palladium at levels higher than unit, using electrochemical set-up, followed by a stabilization process to maintain the hydrogen concentration in palladium lattice stable. In the meanwhile, several measurements of resistance versus temperature have been performed. These measurements have shown several resistive drops in the range of [18K$< T_c <$ 273K] similar to the results presented in literature, when the superconducting phase has been discovered. Moreover, on PdH wires 6cm long the current-voltage characteristic with a current density greater than $6 * 10^4 \ Acm^{-2}$ has been measured at liquid nitrogen temperature. These measurements have the same behavior as superconducting I-V characteristic with sample resistivity, at 77K, of two orders of magnitude lower than copper or silver at the same temperature. The measurements of first and third harmonic of ac magnetic susceptibility in PdH_x system have been performed. These represent a good tool to understand the vortex dynamics, since the superconducting response is strongly non-linear. Clear ac susceptibility signals confirming the literature data at low temperature (9K) and new significant signals at high temperature (263K) have been detected. A phenomenological approach to describe the resistance behaviour of PdH versus stoichiometry x at room temperature has been developed. The value x=1.6 to achieve a macroscopic superconducting state in PdH_x has been predicted.

1 Introduction

1.1 PdH$_x$: overview

Hydrogen (H) and its isotopes dissolve in many metals and occupy interstitial sites in the host lattice producing an expansion of the lattice. Each interstitial H causes displacement of the metal atoms from their original sites while its electrons fill the electronic band of the metal at the Fermi energy level E_F. This gives rise to a series of changes in physical properties of the hosting metal [1, 2]. In this framework Palladium (Pd) is a metal, intensely studied, for much of its peculiarities [3]. Usually it is employed as catalyst for hydrogen reactions [4]. Generally, for Pd the $4d^{10}$ state should be completely filled but in reality the 10 electrons are shared between two zones and the E_F intersects the 4d and the broad 5sp bands [3, 5]. There are 0.36 electrons in the 5sp band [5] and equal number of positive holes of unfilled state in d shell. For this reason Pd absorbs H very strongly. The paramagnetic susceptibility of pure Pd decreases from $550 - 600 * 10^{-6}$ cgs units to diamagnetic behaviour of PdH_x for stoichiometry x =0.75, where x represents the ratio between Pd and H moles [4]. These measurements lead

to deduction that the electron of the H goes into the d shell, thereby the number of positive holes decreases and hence the paramagnetic behaviour diminishes. There is a relationship between the electrical resistance of PdH_x and the H stoichiometric value x (Fig. 1). Analysing the relative resistance $R(x)/R_o$, where $R(x)$ is the PdH_x electrical resistance versus x and R_o is the pure Pd electrical resistance, an experimental pseudo-parabolic curve with negative concavity is observed. At room temperature, this curve has a maximum at $x\approx 0.75$ and then it decreases almost to the initial value at $x\approx 1$. Considering that ideally in the fcc Pd lattice it should be possible to achieve a value x=3 when all the octahedral and tetrahedral sites are occupied, immediately rises the question: *what happens to the electrical resistivity of the PdH at room temperature for x>1?* For low temperatures, with $x\leq 1$ the answer is well known: PdH_x system becomes superconductor [7, 8] with T_c proportional to the x, namely, from x =0.75 with T_c=1K up to T_c=9K for x close to 1. We will attempt a reply to our questions through experimental details.
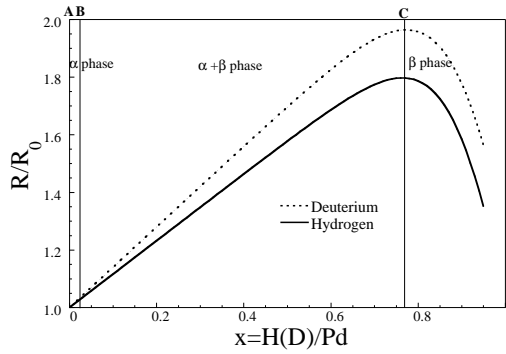
Figure 1. Relative resistance R/R_o versus H stoichiometry $x =$H/Pd (D/Pd) for PdH_x sample (full line) and for PdD_x (dotted line). R_o is the resistance of pure Pd sample at stoichiometry $x =0$.

1.2 PdH_x: thermal coefficient of resistance λ

We have studied the thermal coefficient of resistance λ for PdH_x system. It is well known that the resistance of metallic compounds depends on temperature. For a narrow temperature range, the resistance is described by equation (1):

$$R\left(T\right) = R\left(T_o\right)\left(1 + \lambda\Delta T\right) \qquad (1)$$

where R(T_o) is the resistance of the sample at 0^oC. $\Delta T = T\text{-}T_o$ is the change in temperature and λ represents the temperature coefficient of resistance. From the equation (1) the λ equation (2) is calculated:

$$\lambda = \left(\frac{R\left(T\right)}{R\left(T_o\right)-1}\right) * \Delta T^{-1} \qquad (2)$$

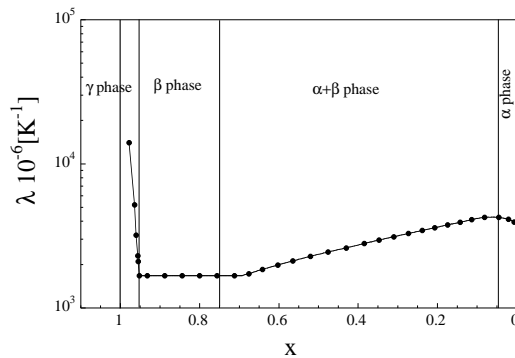where λ expresses the sensitivity of the resistive element versus temperature.

Figure 2. Thermal coefficient λ of PdH_x, in function of hydrogen stoichiometry x [6]. The horizontal axes has been reverted for a better comparison with Fig. 3.
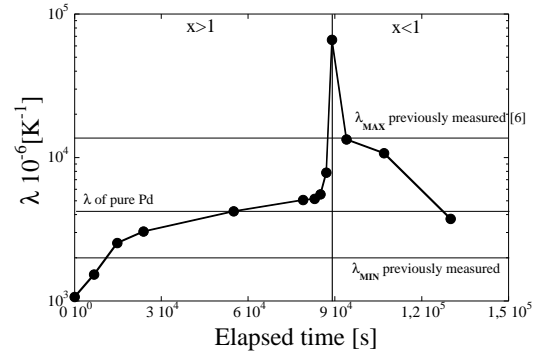

Figure 3. Thermal coefficient λ of PdH_x, in function of time during a slight H deloading (Elapsed time). Each experimental point represents a measurement of λ in the temperature range 273-373K. In these measurements the exact stoichiometry x, is not known, but $x >1$ is present at the beginning of the experiment, i.e. when the elapsed time (τ) is in the range [0s $< \tau < 9 * 10^4$s]. After the H loading the sample was stabilized and measured in temperature as to define λ versus elapsed time while the sample slightly leaks H.

There are contributions to the resistivity other than those due to lattice vibrations. For example, if a second element is present in a metal either as an impurity or as an alloying element, this destroys the periodicity in the electrical potential and gives rise to elastic scattering, hence the resistivity increases. On the other hand, if a short or long range order is present then the resistivity decreases. Clearly the resistivity and in particular λ, are rather sensitive to the order/disorder states [9]. It is well known that λ is also dependent on the variation of stoichiometry x. Pure Pd (Fig. 2) has $\lambda =4000$ppm then it increases to a maximum of $\lambda=4200$ppm at $x\approx0.05$ corresponding to the phase transition between the α and the $\alpha+\beta$ phase. Increasing the H stoichiometry x, λ decreases reaching a minimum of $\lambda=1800$ppm at $x\approx0.75$ corresponding to the phase transition between the $\alpha+\beta$ and the β phase where λ remains constant [4]. Then a steep increase of $\lambda=15000$ppm (Fig. 2) has been measured at about $x\approx1$ [6]. This quasi-asymptotic behaviour shown in Fig. 2 would indicate a possible new phase transition between the β phase and the new γ phase at $x=0.95$ [6].

In Fig. 3 we show further new experimental data demonstrating that with $x >1$ the coefficient λ decreases to lower values, that confirm the presence of the phase transition between the β and the new γ phase [6]. Experimental method to obtain these results is as follows: in the temperature range between the ice melting temperature T_0 and the water boiling temperature T_B, for fixed stoichiometry x, the temperature coefficient of resistance λ can be considered constant, i.e. we assume that in the temperature range $\Delta T=T_B\text{-}T_0$ the slope of resistance versus temperature is constant as claimed in the formula (1). After the loading procedure the sample was cooled to T_0 and the resistance was measured. After that, the sample was warmed to T_B and again the resistance was measured. Using the measured resistance and temperature values, λ has been calculated with equation (2). In order to change the stoichiometry x the sample was immersed

again in the electrolitycal cell in floating configuration to obtain a slight H deloading. This procedure was repeated several times and in Fig. 3 every experimental point represents a measurement of λ in function of the elapsed time during slow H deloading. During these measurements it was impossible to measure the H stoichiometry x in the sample. The only available indication on x is that the stoichiometry is decreasing in time, i.e at elapsed time zero, x is maximum and then it decreases with time. The last three λ points, in Fig. 3, are coherent with λ values for $x < 1$ shown in Fig. 2 [6]. This indicates that the other points in Fig. 3 show λ at very high stoichiometry $x > 1$. In conclusion, in the new γ phase ($x > 1$) the λ value is extremely low, in some cases we have measured a λ as low as 1ppm, whereas close to the transition stoichiometry ($x \approx 1$) λ achieves very high values, up to 66000ppm.
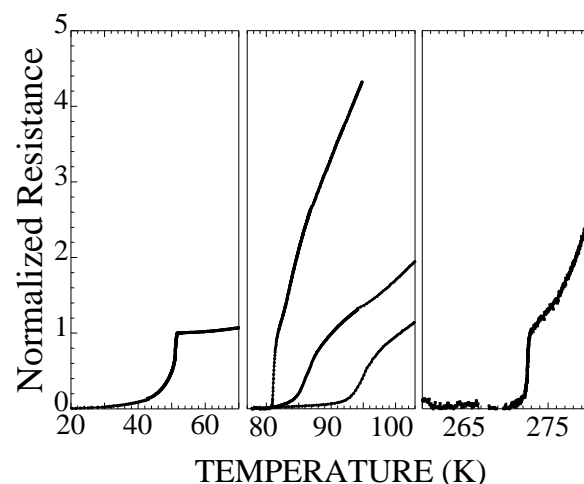

Figure 4. A series of superconducting transitions for PdH_x. The normalized resistance versus temperature is shown, as reported in literature [8].

1.3 PdH$_x$: electrical transport measurements

A series of electrical transport measurements on PdH_x wires, with 50μm diameter, will be presented. Experimental data on the PdH_x behaviour at very high, unexplored, stable H concentration x versus temperature (Fig. 4) shows a resistance drop at T_c=51.6K. Applying 1T dc magnetic field, the resistive drop splits to two lower temperatures of 31.3K and 18.8K [10, 11]. This data renders more consistent, *but not definitive reply to our question*, on the presence of a possible superconducting phase. In the light of this data, we prepared several PdH_x samples with very high stoichiometry x and hence several resistive drops have been measured from 80K up to 273K as shown in Fig. 4. These measured resistance drops, from 5% to 10% of the offset resistance values, have already been published [10, 11]. The presence of these resistance drops for different temperatures T_c indicates different x concentrations in the samples and that only a small fractions of the sample have the x value such as to cause the decreases of the resistance at given temperature. In order to calculate the corresponding x_c values we used the equation presented in Fig. 13. This equation correlates x_c with T_c. Another interesting measurement is the I-V characteristic for a PdH_x sample at LN_2 temperature that shows superconducting critical current greater than $6 * 10^4$ Acm^{-2} (Fig. 5) [10]. The I-V value threshold is by 2 orders of magnitude higher, as we have already underlined in the reference [10]. 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 indicates a rapid resistance increase. As shown in Fig. 5, the effective PdH_x sample resistivity at 77K is 5nΩcm which is lower than copper and silver resistivity at 77K respectively of 300nΩcm and 200nΩcm.
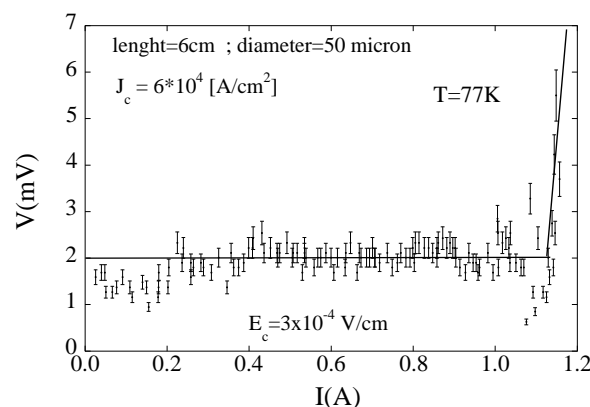
Figure 5. Critical current in PdH_x wire at T=77K [10].

1.4 PdH$_x$: sample preparation

H was loaded into the Pd lattice using an electrochemical cell. This chemical absorption process of H was used preferentially over physical absorption (via H_2 gas pressure) for one primary reason. This method allows higher H/Pd concentrations to be achieved at room temperature and atmospheric pressure in respect to other processes. The cell geometry consists of two parallel Pt square plates (100x100x0.05 mm^3) as anode electrodes, separated by 15cm of electrolyte. The cathode was a Pd sample, placed in the middle between the two anodes. The used Pd samples were thin wires (50μm diameter, lenght in the range 6-30cm) or tapes (50μm thickness, lenght in the range 2-4cm, width 0.4cm). This unusual geometry and a short loading time were adopted to maximize the H loading in Pd cathode and to minimize the transfer of anodically produced species

to the cathode. The attainment of very high loading levels was found to be critically dependent on controlling the impurities in the electrolyte. The electrolyte consisted of strontium sulfate ($SrSO_4$) dissolved in 18MΩcm water (10^{-5} M) giving a slightly acidic solution (5.0≤pH≤6.5). The electrolysis required a dc current from 5mA up to 200mA. During electrolysis the four probe ac resistance measurements of the Pd cathode were taken using an RCL meter at 1mA, 1KHz sinusoidal current. Highly loaded PdH_x samples, were electrochemically stabilised by adding (10^{-5} M) mercurous sulfate (Hg_2SO_4) to the electrolyte. With this procedure the coated cathodes are found to be resistant to H deloading for periods of months at room temperature and pressure. The Pd-Hg "alloy" forms an amalgam that covers the Pd surface and the depth of this "coating" is hundreds of nanometers, so that the effect of the resistance decrease, due to this coating, is negligible.

1.5 PdH$_x$: mean stoichiometry measurement

Important characterization of the sample is the measurement of the average final stoichiometric value x. In order to obtain the x value, it is necessary to know the value of H and Pd moles. Pd moles are measurable with a sensitivity of about 1μmol, but due to the low weight of H moles inside the Pd sample these measurements for hydrogen are not simple. For this purpose we have defined an electrochemical method, destructive however, for the PdH_x sample. Therefore it can only be used as a standard method for the measurement of relative resistance R(x)/R_o versus x as described below. To calculate x we need to evaluate the efficiency ε during the electrochemical H deloading process to avoid the undesired overestimation of x. ε is defined as ratio between the variation of stoichiometry Δx correlated with deloaded H from the sample and the corresponding amount of electrical charge ΔQ transferred through the electrodes:

$$\varepsilon = \frac{\Delta x}{\Delta Q} \qquad (3)$$

For the ε calculation the following experimental evidences are used:

1. the behavior of R(x)/R_o versus x of the PdH_x (fig.1) has 3 experimental constraints:

   (a) point (A) where R(x)/R_o=1 for x=0;

   (b) point (B) that is the separation point between α and $\alpha + \beta$ phase where R(x)/R_o=1.07 for $x\approx$0.05;

   (c) point (C) the maximum of the curve where R(x)/R_o=1.76 for x=0.75;

2. The electric charge Q passed through the electrodes during the deloading of PdH_x samples, proportional to the amount of H moles that exit Pd lattice.

For the average final value x, the following is used:

1. The final value R(x)/R_o achieved during the H loading in Pd (point D Fig. 6);

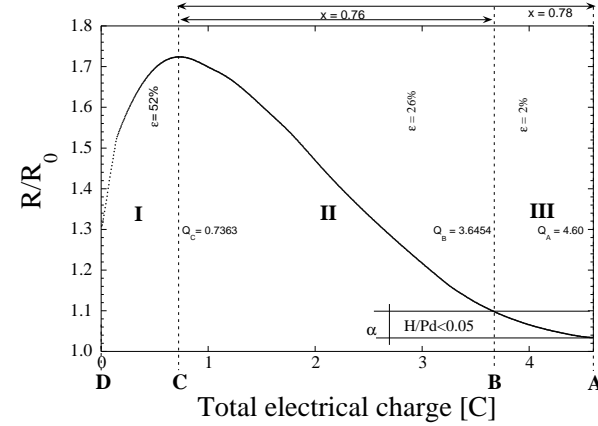2. The estimated efficiency ε value.

Figure 6. R(x)/R_o during H deloading versus electric charge passed trough the electrodes.

During the H loading, electrochemical concurrent processes and long loading time affect the efficiency calculation ε (overestimation) particularly in the zone I (Fig. 6), so that it is necessary to calculate ε during the H deloading. This way ε is underestimated and hence renders acceptable x value. In Fig. 6 the R(x)/R_o during the H anodic deloading in PdH_x wire sample is plotted in function of the total electric charge transferred through the electrodes. The behavior is divided in 3 regions: I in the interval [D-C], II in the interval [C-B] and III in the interval [B-A]. To estimate the ε value we start evaluating the separation point between the zone II and the zone III (point B) which fits the transition point between the α and $\alpha + \beta$ phase. The electric charge necessary to change the R(x)/R_o from the value 1 (point A) to 1.07 (point B) is ΔQ=1 Coulomb. Comparing this experimental data with the data in item 1(b) we find that the efficiency is ε=5%, which is way too low. The H stripping dynamics is dominated by two processes: the superficial recombination and the H diffusion from the inside to the surface of the Pd. Since the ε is determined only by the superficial recombination and in the zone III the diffusion effect is dominant, the underestimation of the ε occurs in this zone. Therefore the zone II must be considered for a more accurate evaluation of ε. In the interval [C-B] the electric charge is ΔQ=2.8 Coulomb and comparing this data with the items 1(b) and 1(c), we find an efficiency of ε=26%. In the zone I the sample is overloaded with H. Initially, around the point (D) the deloading efficiency is ε=100% until the change of the slope (Fig. 6), to arrive to ε=26% at the point (C). We presume that the average efficiency is 52% in this zone (doubled efficiency of the zone II) which is still strongly conservative estimation in respect to the arithmetic mean value (ε=63%).
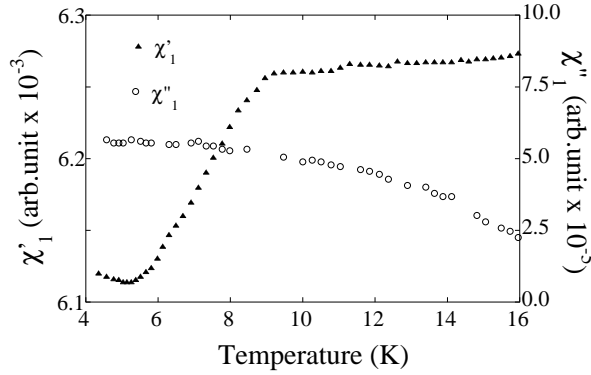
Figure 7. Real (triangles) and imaginary (circles) part of first harmonic (H_{ac}=6G f=1KHz) of PdH_x slab (x≈1).
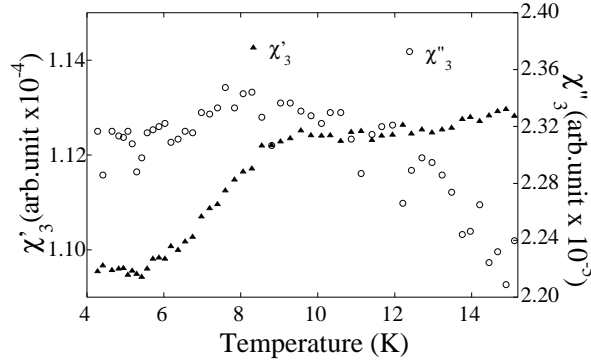

Figure 8. Real (triangles) and imaginary (circles) part of third harmonic (H_{ac}=6G f=1KHz) of PdH_x slab (x≈1).

From this definitive ε value we obtain the final mean x value. The electric charge in the zone I, from the point (C) to the point (D), is ΔQ=0.8 Coulomb. Hence the mole number of the H entered in the sample for the zone I, considering ε=52%, gives Δx=0.4. Now, as stated in item 1(c), the stoichiometry of the sample is Δx=0.75. Therefore the final stoichiometry is $x_f \geq 0.75 + 0.4 = 1.15$. Resuming this procedure, there are two important implications. First of all, this method is general and valid for any sample geometry. Secondly, it is independent from any concurrent electrochemical processes and from Pd sample moles.

2 Results and Discussion

To further define the possible superconducting properties of PdH_x at high temperatures, we have performed and are presenting in this paper, the measurements of ac magnetic susceptibility and its higher harmonics. It is extremely important to check the presence of high harmonics since the superconducting response is strongly non-linear. In fact in the following section 2.1, we will discuss the first and third harmonic of the ac magnetic susceptibility measurements, moreover in section 2.2 a possible simple phenomenological approach that explains the PdH_x relative resistance in function of x at fixed temperature (300K) will be presented.
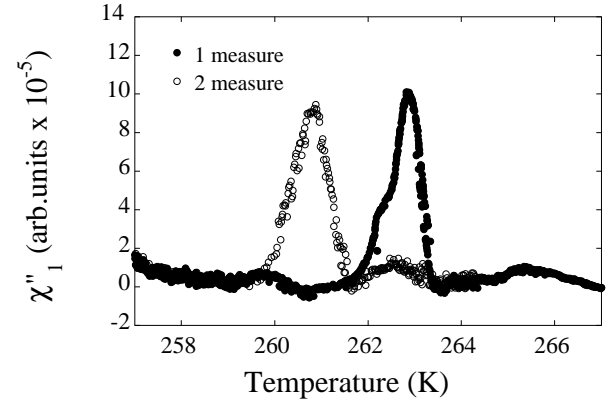

Figure 9. Imaginary parts of first harmonic of PdH_x slab, first measure (full circles), second measure after 1 week (empty circles) (x >1).

2.1 ac susceptibility measurements

The ac magnetic susceptibility ($\chi_n = \chi_n^{'} + $ i $\chi_n^{''}$: n=1,3) measurements were performed with the European Facility 8T flow cryostat [12]. This cryostat has a susceptometer with an in-line double pick-up coil (Helmotz like) bridge with an exciting external ac magnetic field up to 6G at frequency in the range [31Hz<f<2kHz], able to acquire with a lock-in amplifier the first seven harmonics of ac magnetic susceptibility, with the possibility to use a dc magnetic field up to 8T. The sample was cooled down to LHe temperature in ZFC (Zero Field Cooling) then the temperature has been slowly increased up to 300K. The data file collects the experimental value of ac susceptibility as the average value of 5 points while the temperature is not varied more than 0.01K. The subtraction of the null file due to the measurement system has been performed.

Some consideration on the phase measurement of the sample must be done for clarity. Usually in the ac magnetic susceptibility measurements the phase of the signal is imposed in order to maximize the in-phase ($\chi_1^{'}$) component and minimize the out-phase ($\chi_1^{''}$) component when the sample is in superconducting or normal state (zero-phase procedure). In this case we minimized the imaginary part at LHe temperature. In Fig. 7, the real $\chi_1^{'}$ and the imaginary $\chi_1^{''}$ components of the first harmonic are plotted at low temperature and a T_c of 9K [7] is shown. In Fig. 8, the third harmonic $\chi_3^{'}$ and $\chi_3^{''}$ shows similar behavior of the sample. This indicates the presence of the well-known superconducting phase at low temperature. This superconducting phase, in accordance with literature data, is achieved for a stoichiometry x≈1 [7]. In Fig. 9 (first measurement) a very significant signal of the imaginary component $\chi_1^{''}$ is shown at 263.5K, corresponding to zones of PdH_x with stoichiometry x>1. A week later, the same measurements were repeated on this PdH_x sample (second measurement), shown in Fig. 9, and the critical temperature shifted down

to lower temperature T_c=261.5K (slight deloading, probably due to thermal cycles). A clear diamagnetic signal of the real component χ_1' is shown in Fig. 10, overlapped with an extensive paramagnetic signal due to the PdH_x zones with stoichiometry in the range $[0 \leq x < 0.75]$ [4, 13]. This indicates that only a small fraction of the PdH_x sample has the appropriate stoichiometry $x >1$ corresponding to the superconducting phase at this critical temperature T_c=263.5K. This slope recalls the magnetic susceptibility behavior of the $RBa_2Cu_3O_{7-x}$ with paramagnetic ordered rare earths (R=Sa,Eu,etc.) where, decreasing the temperature well below T_c, the behavior changes from diamagnetism to paramagnetism [14].
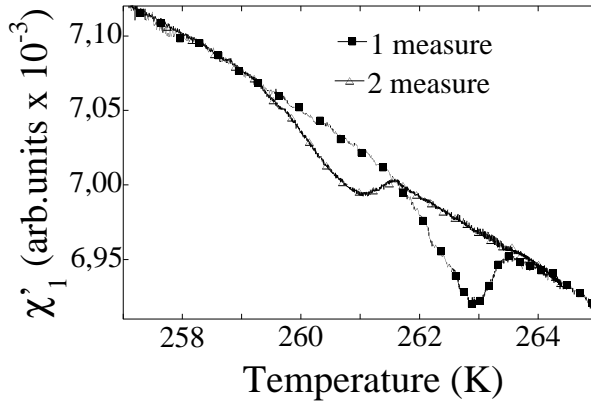

Figure 10. Real parts of first harmonic of PdH_x slab, first measure (full squares), second measure after 1 week (empty triangles) ($x >1$).
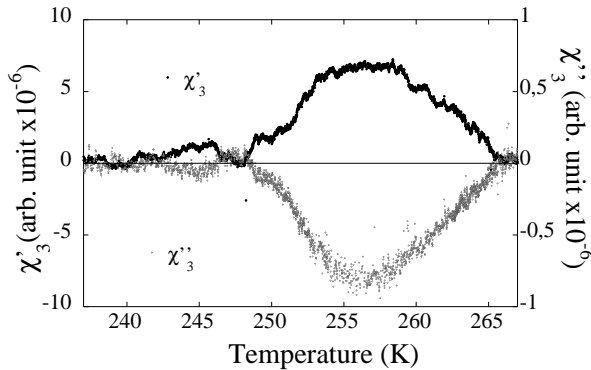

Figure 11. Real and imaginary parts of third harmonic of PdH_x slab (first measure).

The fact that χ_1' signal has a value lower than expected (about 1/6 less) in comparison with the imaginary component χ_1'', can be imputed to the non-appropriate zero-phase procedure, in fact, the imaginary component has been minimized at 4.2K and this procedure is strongly dependent on the temperature. We checked the presence of the third harmonic and in Fig. 11 the third harmonic real and imaginary part of first measure show a clear oscillation with an onset

temperature of 264K. These results have been obtained after two months (room temperature and pressure) storage of these highly H loaded PdH_x samples and the same sample rendered nearly the same T_c in three consequent measurements.

2.2 R/R_o **H loading at 300K: a phenomenological approach**

The behaviour interpretation of the relative resistance R/R_o at 300K in function of x content, uses the concept of the two phases (α,β) and their coexistence ($\alpha+\beta$) in the PdH_x system [3] but since H is not a parent metal of Pd, this approach is not applicable. As shown in Fig. 12, a phenomenological model has been developed. The model predicts that R/R_o of the PdH_x systems at room temperature will exponentially decrease with the increasing of H loading x for $x>1$. Moreover, it predicts that R/R_o will decrease to zero resistance at x_c=1.6, so that the PdH_x will be in a room temperature superconducting state. The PdH_x system is modelled as having two electron transport mechanisms available in parallel: one superconducting fluctuation transport and the other normal transport. In other words, their corresponding resistances are in parallel to obtain the overall resistance.
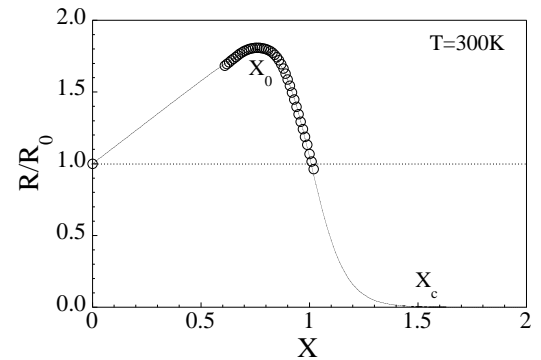

Figure 12. The best fit of experimental data for PdH_x sample using the parallel model of the relative resistance. A critical temperature T_c =300K is achieved at x_c=1.6. The x_o represents the H stoichiometry where the relative resistance is at maximum value.

The normal electron transport mechanism is modelled to describe a relative resistance that linearly increases with the stoichiometry x. This linear dependence is believed to result from the linear increase in the number of scattering centres in the system with the increase of x. Thus, the relative resistance is written as:

$$\left(\frac{R}{R_o}\right)_l = 1 + \Lambda x \quad (4)$$

where R is the resistance at stoichiometry x, R_o is the resistance of a pure palladium and Λ is a constant of proportionality. The superconducting fluctuation transport mechanism

is modelled to describe a relative resistance that exponentially decreases with x. This exponential dependence for $x>1$ is written as:

$$\left(\frac{R}{R_o}\right)_e = \beta e^{-\gamma(x-x_o)} \tag{5}$$

where R and R_o are as defined in Eq. 4, β is correlated with the frequency described in the superconducting fluctuation theory [15]. γ is the ratio between the free energy increment [15] or the condensation energy of the superconducting domains and the Boltzmann factor kT at 300K. $(x- x_o)$ represents the number of fluctuating superconductive domains for x in the range $[0.75<x<x_c]$[16].

This superconducting fluctuation process can be explained as follows: During the H loading, the H electron fills the unfilled 4d state easily without affecting much the E_F level due to the high electron state density in 4d shell. Increasing H stoichiometry, the electrons fill the unfilled 5sp bands above the 4d bands. Due to the low electron state density of 5sp band, the E_F must be raised. This leads us to deduce that the dissolved H atoms in Pd are completely ionised (H^+) in interstitial position without being specifically bound to a particular Pd atom. The dissolved H^+ ions [5] are also extremely mobile. The transition rate is 10^{12} s^{-1} and the self-diffusion coefficient is 10^{-6} $cm^2 s^{-1}$. H^+ ions localized in a cluster, in average remain about their sites for 10 oscillations before moving to nearest-neighbour sites. Meanwhile, the sub-lattice vibrates with very high localized optical frequencies at about 10^{13}Hz, due to the lightness of the H mass. In this context a local fluctuation of superconductivity in PdH_x can occur with a rather unusual coupling between localised optical phonons and the E_F electrons that spent considerable time around H^+ ions. This combination allows the electrons at E_F level to experience the attraction through H-sub-lattice (BCS like approach). Increasing H content, the number of clusters and local superconducting fluctuations increases achieving the complete superconducting phase.
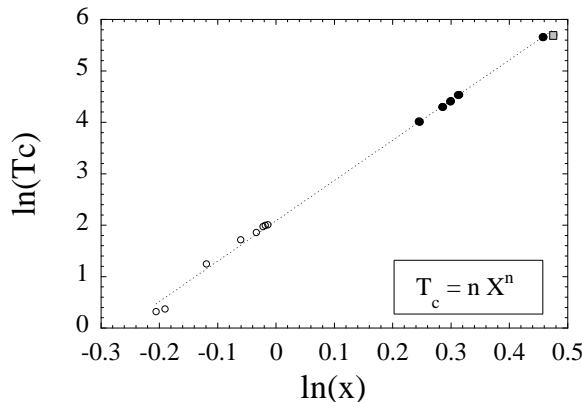

Figure 13. Experimental stoichiometry x data for PdH_x samples with low T_c [7] (empty circles) together with our phenomenological approach datum (gray square). In accordance with this model, x values for a series of experimental T_c shown in Fig. 4, have been printed as full circles.

Adding the relative resistances from Eq. 4 and Eq. 5 in parallel, one obtains a phenomenological expression for R/R_o at room temperature as a function of x:

$$\left(\frac{R}{R_o}\right)_p = \frac{(1 + \Lambda x)\,\beta e^{-\gamma(x-x_o)}}{1 + \Lambda x + \beta e^{-\gamma(x-x_o)}} \tag{6}$$

Using the fitted free parameters, the resulting curve is shown in Fig. 12. The best fit of equation (6) produces the final equations (7,8):

$$\left(\frac{R}{R_o}\right)_l = 1 + 1.16x \tag{7}$$

$$\left(\frac{R}{R_o}\right)_e = 40e^{-12.4(x-0.76)} \tag{8}$$

In equation (7), the parameter $\Lambda=1.16$ is strictly correlated with the linear lattice expansion during H loading [1]. From equation (8) the condensation energy of 270meV for the superconducting phase can be calculated at $x=x_c$. This value is in the expected range for the formation energy of coherent systems. The equations 6-8 render the value $R=0$ for $x_c=1.6$. This indicates a possible superconducting state at 300K for $x_c=1.6$. This datum (gray square in Fig. 13) together with the experimental data at low T_c (empty circles in Fig. 13) reported in literature, are used to extrapolate the relationship in Fig. 13: $T_c=nx^n$. For PdH_x system results $n=7.86$. Using this relationship we added the resistance drops data (Fig. 4) to the plot in Fig. 13 (full circles) to obtain a quantification of the mean stoichiometry x that results in the range $[1.27 < x_c < 1.57]$.

3   Summary and conclusions

This letter presents first and third harmonics of ac susceptibility data together with our previous variety of experimental data [10] on electrical transport. These measurements together with several resistive drops in the temperature range $[51.6K < T_c < 273K]$ give some further indication to answer the question: *what happens at room temperature for $x>1$ in PdH_x system?* Should the PdH_x system with $x>1$ be a HTSC, the presented data must be confirmed with a clear Meissner effect measurement. Nevertheless, a small diamagnetic signal of $\chi_1^{'}$ at 263K in coincidence with imaginary part of $\chi_1^{''}$ and real and imaginary part of third harmonics have been measured. A simple phenomenological approach based on the parallel of two electric transport mechanisms in order to explain the R/R_o behaviour at room temperature in the PdH_x system as a function of the H concentration x has been developed. The first mechanism explains the experimental increases of the relative resistance in the PdH_x system due to the lattice expansion in the range $[0<x<x_o=0.75]$. The second mechanism explains the decreases of the PdH_x relative resistance at $x>x_o$, as a typical expression of the superconducting fluctuations of resistance. The superconducting state at room temperature $T_c=300K$ for concentration $x_c=1.6$ has been predicted.

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