

Measurement of Heat Capacity of PdH_x

Luca GAMBERALE¹, Daniele GARBELLI, Giuseppe PIANA
Pirelli Labs – Materials Innovation, v.le Sarca 222, 20126 Milano, Italy

Abstract

We present experimental data on heat capacity and thermal coefficient of resistance of PdH_x system at loading ratio $0 < x < 0.93$ at room temperature. To this purpose a dynamic measurement method has been devised. Data confirm the existence of a phase transition around $x \simeq 0.7$ (γ phase).

1 Introduction

Despite the enormous increase of work in the study of the PdH_x system in the last few years, there has not been (to our knowledge) a systematic study of heat capacity of the PdH_x system at loading ratio in the range $0 < x < 0.93$ at room temperature. The present work is addressed to the measurement of such a quantity. It is possible to define a “molar” heat capacity C_{PdH_x} as the ratio:

$$C_{PdH_x} = \frac{\text{Total heat capacity}}{\text{moles of Pd}} \quad (1.1)$$

without entering in the subtle issues raised by this problem; the present work will be kept on an eminently experimental ground.

Our measurement was made possible by the availability of a method for loading and keeping charged a thin Pd wire for a long time [1-3]. The method relies on an electrolytic procedure (based on Sr and Hg deposition on the Pd cathode) able to reach high loading ratio ($[H]/[Pd] \approx 1$). The samples used are Pd wires 50 μm diameter, 10 cm length Pd wire. The stability of the loading is guaranteed by the presence of a thin Hg layer (typically a few μm) electrolytically deposited on the Pd wire surface. Depending on the Hg layer thickness we are able to obtain a totally blocked or slowly deloading wire (<10% deloading in one day).

Due to the smallness of the sample, when measuring heat capacity we are faced with two main problems:

1. devising a reliable method for measuring wire temperature
2. avoiding large heat leakage from the sample.

We have solved these difficulties by measuring the time variation of the wire temperature due to step-wise current pulses by monitoring the electric resistance.

Heat leakage from the sample due to the presence of air has been reduced by placing the wire sample inside a vacuum chamber (pressure ~ 60 mTorr) and soldered to two vacuum-tight electrodes kept at ambient temperature. We have verified that, in this pressure range, residual leakage is significantly reduced.

Heat capacity has been measured at several loading ratios. This has been accomplished by progressively deloading a highly loaded Pd wire ($x \simeq 1$), either by spontaneous deloading (especially at high loading ratios) or by a suitable heating of the wire obtained by current pulses.

2 Temperature measurement

The loading ratio was estimated by measuring the electrical resistance of the wire [4].

The relation between resistance and temperature is

$$R(x, T) = R_0(x)(1 + \alpha_r(x)T) \quad (2.1)$$

The measurement of the thermal coefficient of resistance $\alpha_r(x)$ was performed at several loading ratios in the range $0 \leq x < 0.97$ and on different wires by measuring the wire resistance (using a four wire method) at three different temperatures (15°C, 25°C and 35°C) at fixed loading ratio. This was accomplished by placing the wire in a sealed container into three different water heat baths. The obtained results are summarized in Figure 1.

¹ E-mail: luca.gamberale@pirelli.com

Data are consistent with available data in the literature [5, 6] and confirm the validity of equation (2.1) in the range $0 \leq x < 0.97$. It is worth noting that the presence of the Hg layer ($\sim 2\mu\text{m}$), on the Pd surface, does not alter significantly the measured resistance values since its resistivity ($\sim 10^{-6} \Omega \text{ m}$) is much larger than that of Pd ($\sim 10^{-7} \Omega \text{ m}$) and the cross section ratio is $\sim 6 \cdot 10^{-3}$.

3 Physical model of the wire

The temperature distribution along the wire due to Joule heating cannot be uniform because the wire ends are kept at room temperature. Therefore it is necessary to develop a physical model that accounts for spatial dependence of the wire temperature. The model is based on the following assumptions:

- the wire is homogeneously loaded with hydrogen,
- the radial temperature gradient on the wire is negligible.

These assumptions lead to the following partial differential equation (see [7]):

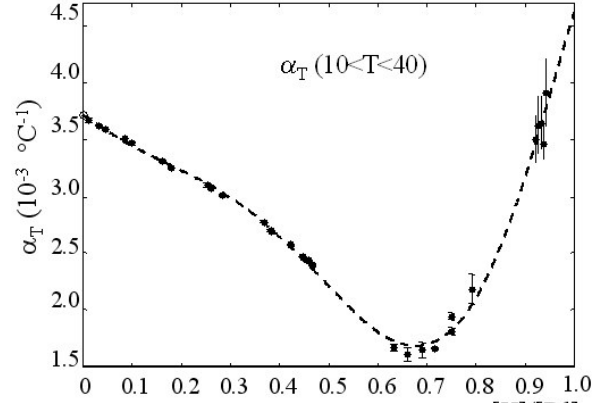


Figure 0: Thermal coefficient of resistance as a function of hydrogen loading.

$$LK_T \frac{\partial^2 T}{\partial x^2}(x,t) - C_T \frac{\partial T}{\partial t}(x,t) - (G_T - \alpha_T R_0 I^2) T(x,t) + R_0 I^2 + G_T T_{amb} = 0 \quad (3.1)$$

where $T(x,t)$ is the wire temperature at position x at time t , K_T is the longitudinal thermal conductivity of the PdH_x wire, G_T is the transverse thermal convection coefficient, I is the current across the wire, T_{amb} is the ambient temperature, L is the wire length and C_T is the total heat capacity of the wire. Please note that the radiative contribution to the dissipation power is neglected due to its smallness with respect to the convection term.

Being the heat capacity of the connectors holding the Pd wire much larger than C_T , we are allowed to fix the spatial boundary conditions of the problem as

$$T\left(\pm \frac{L}{2}, t\right) = T_{amb} \quad (3.2)$$

Besides, the initial condition is given by the steady state of the wire traversed by a constant current I_0 present prior to the pulse i.e. the stationary solution of (3.1) for $I = I_0$. The solution of the analytical problem is addressed in [7] where $T(x,t)$ is calculated. Then the wire resistance $R(t)$ as a function of time (the actual physical measured quantity) is given by the spatial integral:

$$R(t) = \int_{-\frac{L}{2}}^{+\frac{L}{2}} \frac{R_0}{L} (1 + \alpha_T T(x,t)) dx = R_{I_0} + \frac{2\sqrt{2}R_0\alpha_T}{\pi C_T \sqrt{L}} \sum_{n=1}^{\infty} (-1)^{n+1} \frac{\beta_n \tau_n - \beta_{0n} \tau_{0n}}{2n-1} \left[\exp\left(-\frac{t}{\tau_n}\right) - 1 \right] \quad (3.3)$$

where R_{I_0} is the steady-state wire resistance when a current I_0 is passing through the wire,

$$\beta_n = (-1)^n (1 + \alpha_T) R_0 I^2 T_{amb} \frac{2\sqrt{2}L}{(2n-1)\pi}, \quad (3.4)$$

$$\tau_n = C_T \left[G_T - \alpha_T R_0 I^2 + \frac{K_T}{L} (2n-1)^2 \pi^2 \right]^{-1}$$

and β_{0n} and τ_{0n} are obtained by the substitution $I \rightarrow I_0$ in (3.4).

It is possible to show that to a good approximation only the first two terms in the sum of eq. (3.3) give a significant contribution in our experimental conditions.

4 Experimental setup

The experiment consists in a wire suspended inside a vacuum chamber and connected through vacuum-tight connectors to a current generator (ELIND 500KL2,4/6). Three digital multimeter (Keithley2000) measure the voltage across the wire, the current through the wire and the ambient temperature by means of a Pt100 thermoresistance. A computer at a rate of 5-10 samples/second continuously acquires data. The PC also controls the current generator via GPIB and stores the data on a file for further elaboration. The vacuum chamber is continuously evacuated by a rotative pump and it is maintained at a constant pressure of ~60 mTorr. This procedure is necessary in order to reduce heat leakage through the surface of the wire that would otherwise considerably reduce the accuracy in the estimation of C_T . Secondly the time constant of the system is also increased to a suitable level for the available sampling rate.

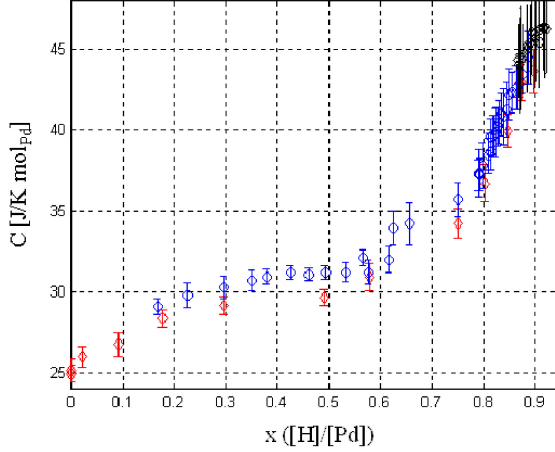


Figure 2 Heat capacity per mole of Pd of the PdH_x system as a function of hydrogen loading.

5 Results

The best estimation of C_T has been computed as the weighted average over about 10 different current steps. Please note that the loading ratio was not affected by the current steps used in the measurement since restoring the current to the initial value the resistance returned to the initial value.

The only unknown parameters in our system (eq. (3.1)) are C_T , K_T and G_T and have been estimated numerically by fitting the data with the least squares method.

The actual function used in the fitting procedure is the simplified expression for the wire resistance as a function of time given by the first two terms of the sum in equation (3.3), whose analytical expression is

$$R(t) = R_0 + A_1 \left(1 - \exp\left(-\frac{t}{\tau_1}\right) \right) + A_2 \left(1 - \exp\left(-\frac{t}{\tau_2}\right) \right) \quad (5.1)$$

where R_0 is the wire resistance before the current pulse while the coefficients A_1 , A_2 , τ_1 and τ_2 have a well defined dependence on the system parameters².

The goodness of the measurement and, in particular, the validity of the assumptions at the basis of the theoretical model, have been tested by measuring the heat capacity of pure Pd and Pt wires in the same conditions. The values found are consistent with the well-known published data³.

The value of C_T obtained by fitting the data is not the heat capacity of the PdH_x but rather the total wire heat capacity and is the sum of two contributions:

$$C_T = C_{PdH_x} + C_{Hg} \quad (5.2)$$

where C_{PdH_x} is the heat capacity of PdH_x system and C_{Hg} the heat capacity of the Hg surface layer. Two different methods have been used for the estimation of C_{Hg} :

1. evaluation of the quantity of Hg deposited on the wire by measuring directly the Hg thickness by means of SEM images;

² $A_1 = \frac{2\sqrt{2}R_0\alpha_T}{\pi C_T \sqrt{L}} (\beta_{01}\tau_{01} - \beta_1\tau_1)$ and $A_2 = -\frac{2\sqrt{2}R_0\alpha_T}{3\pi C_T \sqrt{L}} (\beta_{02}\tau_{02} - \beta_2\tau_2)$.

³ The main source of uncertainty in C_T is introduced by the thermal coefficient of resistance $\alpha_T(x)$.

2. comparison of the C_T value of PdH_{x=0} sample covered with Hg layer with the C_T value of a pure Pd wire.

The two methods give consistent results within the accuracy of the overall measurement⁴. In order to avoid the trivial dependence of C_{PdH_x} from the size of the sample, we have defined a specific heat capacity:

$$C(x) = \frac{C_{PdH_x}}{n_{Pd}}, \quad (5.3)$$

where n_{Pd} is the number of Pd moles in the sample.

In Figure 2 are represented the measured $C(x)$ of three different wires.

6 Conclusions

The striking feature of Figure 2 is the rapid variation of $C(x)$ around $x \approx 0.7$. Such a behavior of the heat capacity suggests the existence of a phase transition. This hypothesis is supported by the observation that a similar trend is shared by other physical quantities like the thermal coefficient of resistance α_T (measured in the present work, Figure 1), resistivity [4, 6], superconducting behavior [8], Hall coefficient [9], diffusion coefficient [10] and volumetric dilatation coefficient [11]. Moreover, the existence of such a phase transition has been recently predicted by a theoretical model [12, 13].

As a final remark, as previously observed, also K_T and G_T are determined by the fit. Although K_T would be a significant quantity, characteristic of the PdH_x system, unfortunately its determination is affected by very large error bars. Lastly, the parameter G_T is not relevant because it is not an intrinsic characteristic of the PdH_x system. In fact it depends on residual pressure and on geometrical configuration of the experimental setup.

7 Acknowledgments

We are indebted with Prof. G.Caglioti for his continuous support during the development of this work. We also acknowledge Dr. F.Celani for the discussion and suggestions about the loading procedure.

8 References

- [1] F.Celani et al, submitted to *Phys. Lett. A*, (preprint: [http://wwwsis.lnf.infn.it/pub/LNF-00-006\(P\).pdf](http://wwwsis.lnf.infn.it/pub/LNF-00-006(P).pdf)).
- [2] F.Celani et al, , *Proceedings of ICCF8*, pag 181.
- [3] A.Spallone et al, , *Proceedings of ICCF8*, pag 191.
- [4] D. Azzarone, D. Garbelli, F. Fontana, *Proceedings of 4th Asti workshop on Anomalies in Hydrogen/Deuterium loaded Metals*, ed. W. J. M. F. Collis (1999).
- [5] J.C. Barton, F.A. Lewis and I. Woodward (1963), *Trans. Faraday Soc.* **59**, 1201.
- [6] P.Tripodi et al., *Phys. Lett. A.*, 276, 122-126 (2000).
- [7] D.Garbelli, G.Piana, L.Gamberale, submitted to *Phys. Lett A*.
- [8] B.Stritzker, H Wulh, *Hydrogen in Metals I*, Cap 6, vol 28, Topics in Applied Physics Springer-Verlag Berlin-Heidelberg (1978)
- [9] R. Wisniewski, A. J. Rostoscki, *Phys.Rew B3*, 2 251-252(1971)
- [10] F.Taddei, Thesis, "Analisi teorica del sistema palladio idrogeno", Università degli studi Milano-1995 (in italian).
- [11] B.Baranowsky, S. Majchrzak and B.Flanagan, *J.Phys.F.*,vol.1, 258,(1971)
- [12] G.Preparata, *QED coherence in matter*, World Scientific (1995)
- [13] G.Preparata, M.Cola; E.Del Giudice, A. De Ninno, *Proceedings of ICCF8*, pag 349.

⁴ the actual value of C_{Hg} depends on the specific sample under consideration. However its magnitude is of the order of 6-8% of C_T .