

Letter

Answer to the remarks on superconductivity in PdH

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ABSTRACT

This is the answer to the letter of Baranowski and Dębowska [Baranowski and Dębowska, J. Alloys Compd. 437 (2007) L4–L5].

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With this letter we would like to expose our understanding on superconductivity of PdH system. Some short elucidations on our first three cited papers in the Baranowski and Dębowska letter [1] and some consideration on the PdH electrical resistance in particular to the *I*-*V* measurements are done. We also recall observations in our further published papers containing important magnetic measurements and detailed explanations on the superconducting properties of PdH system and we dedicate some notes on interstitial site occupancy at 300 K with additional information on electrolysis at room temperature and pressure.

We wish to underline that the scientific work described in all our published papers have been peer reviewed by referees as decided by the editors of journals since the work has been presented at international conferences and workshops in the superconductivity field.

In our first letter on PdH system [2], indications of new phase transition in PdH system loaded at very high H stoichiometry have been found. The steep variation of the resistivity temperature coefficient in a short range of stoichiometry represents a strong evidence of a phase transition in PdH.

In other two papers [3,4], the high T_c superconductivity (HTS) phases in PdH samples are shown and analyzed. Obviously these initial experimental studies are incomplete because the Meissner effect is not shown.

The first point of the letter Baranowski/Dębowska [1] remarks "...small changes in PdH resistivity...". It must be underlined that the resistance behavior versus temperature in magnetic field is

what expected in a superconducting resistivity transition: a shift of the transition to lower temperature. More significant is the *I*-*V* characteristic at 77 K of the wire PdH sample, where increasing the electrical current passing through the PdH sample, the expected voltage drop increase is not present, very similar to the superconducting critical current behavior while the sample is in superconducting phase. The *I*-*V* plot shows the specific current amplitude (critical current value I_c) where the superconductivity breaks and voltage increases. We underline that the PdH resistivity has a value of 5 nΩ cm better than copper and silver at 77 K (300 nΩ cm and 200 nΩ cm, respectively).

Following this issue, other three further important papers on magnetic measurements [5–7] have been published. The paper [5] is a review on the PdH samples preparation, temperature coefficient resistivity measurements, resistance measurements, a phenomenological model and some ac susceptibility magnetic data. In these last three papers [5–7] new and significant tests of the HTS phases in our PdH samples have been shown. In particular the following items:

- (A) Meissner effect at the transition temperature, "the signature of superconductivity". This diamagnetic signal is proportional to the ac susceptibility first harmonic real part [8];
- (B) energy dissipation at the transition temperature connected to the critical current value using the 'critical state model' that is proportional to the ac susceptibility first harmonic imaginary part [8].

It is well known that these transitions be superconducting, the magnetic response must be strongly non-linear and the ac magnetic susceptibility signal is non-harmonic [8], hence

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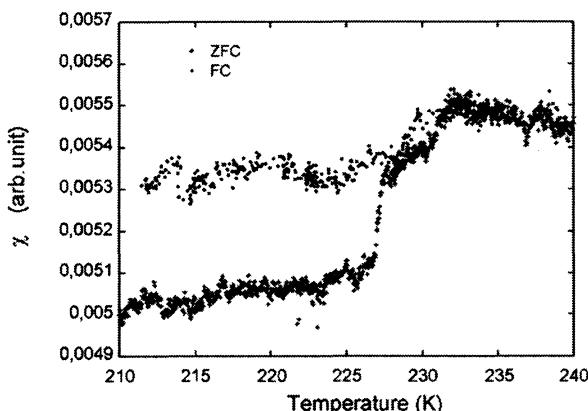


Fig. 1. FC, ZFC measurements of ac first harmonic real component of PdH_x phase at 235 K.

(C) high harmonic ac susceptibility components are present. Two important aspects regarding the perfect diamagnetism of the superconductors, the flux exclusion underlined by the zero field cooling (ZFC) and the flux expulsion (Meissner effect) underlined by field cooling (FC) [9], have been measured in PdH samples. In superconducting materials with strong pinning (important for the critical current amplitude) the FC signal is lower than the ZFC. This is because the pinning prevents the vortices motion and the presence of internal magnetic fluxon field in the sample decreases the superconducting diamagnetic signal:

(D) ZFC and FC ac susceptibility measurements show the Meissner effect in PdH as shown in Fig. 1.

Furthermore, other authors have published papers showing HTS- PdH phases on PdH samples produced and measured in different way in respect to our loading procedure and measurement apparatus [10–12].

Second point of Baranowski/Dębowska comment letter [1], considers the two different vacancies: octahedral and tetrahedral in palladium and their filling at $T = 300$ K.

In literature data [13] the interstitial sites occupation by hydrogen ions, which necessarily constitute a finite population in any one specimen, leads to a thermodynamic description of the dissolved hydrogen in terms of Fermi–Dirac statistic. Thus, the activity a , of the dissolved hydrogen must be expressed more generally than by equation

$$\mu = \mu_0 + RT \ln a$$

here, μ is the chemical potential, μ_0 is the chemical potential of pure specimen with $x = 0$, and recording that

$$a = \gamma x$$

x is the mole fraction of the component in solution and γ is the activity coefficient

$$\mu = \mu_0 + RT \ln \gamma \left(\frac{x_1}{1 - x_1} \right)$$

$x_1 = n_H/n_O$, with n_H is the number of dissolved hydrogen atoms and n_O is the number of interstitial positions of the class that produces the lowest Gibbs-free energy state. In the fcc Pd lattice there is one octahedral interstitial site and two tetrahedral sites per Pd atom, subscript index O would represent octahedral positions.

The important consequence of this approach is that as $x_1 \leq 1$ the chemical potential, μ , of the interstitial hydrogen raises to very large values. Indeed, the source of the hydrogen cannot have a suf-

ficiently high chemical potential to cause the filling of all of the lowest-energy class of sites. Therefore, a sufficiently large μ would cause the next-higher energy class of interstitial sites to become partially populated at $x_1 < 1$. In the case of palladium one would predict some tetrahedral site (T) occupancy at x_1 (octahedral) < 1 , so that for $x \sim 1$ at 300 K the tetrahedral interstitial sites are occupied.

Third point of Baranowski/Dębowska comment letter [1] underlines that electrochemical charging is not always well controlled.

Provided that for all the steps: materials, solutions, preliminary and post-H-loading treatments, clean room, etc. are reverent to the ‘integrated micro-electronic standard industry procedures’ the electrochemical hydrogenation process can be well controlled.

Fourth point of Baranowski/Dębowska comment letter [1] cites that the electrode potential of the charged palladium sample is of little importance, as clear non-equilibrium conditions are present on the electrode surface, and therefore, the electrode potential has practically no direct correspondence to equilibrium conditions.

As cited in the book [14]: “in electrochemistry the equilibrium is not static business, as it often seems to be from thermodynamic, in particular it is better to regard it as a two-way traffic of ions and electrons across the interface and at the equilibrium potential the rate of exchange in each direction is equal in magnitude though opposite direction. The situation is not trivial as in gas-phase adsorption where gas particles stick to the solid surface and the solvent for the gas particles is vacuum an inert, indifferent and non-interfering solvent”. In electrochemical process there are arrangements of ions, dipoles, neutral molecules and in the electrode/solution interface, a double-layer electric charge distribution is present. But this task is resolvable: the criterion of thermodynamic equilibrium between two phases for an interface is the equality of electrochemical potential. This is done with the use of a third non-polarized interface in the solution, called reversible hydrogen electrode as reference (platinum electrode immersed in H_2 gas bubbles). The Tafel–Volmer equation [15] considers the polarization processes connected to non-equilibrium. The central term, called overpotential η , is referred to the electrode potential displacement from its equilibrium value. In Tafel–Volmer process, two overpotential components are considered, the Volmer component, η_1 , due to the polarized behavior, and the Tafel component, η_2 , referred to the hydrogen dissolution into bulk metal. In the case of quasi-equilibrium it is useful to speak of an effective fugacity of the incoming hydrogen. In fact, at steady state, such that the surface population everywhere on the metal surface and the concentration of hydrogen within the metal is uniform and independent of time, then one can say that there is thermodynamic equilibrium among all of the states of hydrogen within and upon the surface of the metal, but not between these states and the source of the hydrogen. In these circumstances, the homogeneously lattice-dissolved hydrogen at concentration x , can be related to the effective fugacity f , as in the equilibrium condition of molecular hydrogen gas at the same temperature and same concentration x . We must bear in mind that the H atoms within the metal, experience only the mechanical retort from the lattice. There is no external pressure p_{H_2} correlated with f , and in particular there is no force tending to push H atoms to smaller separations or to cause double occupancy of any one interstitial site. This process is only due to the statistic occupation of hydrogen ions in the interstitial sites. It can be assumed only that the functional relationship of the electrochemical process is identical with f/H_2 of the gas process. The steady state situation is achieved using galvanostatic transient technique [15]. This technique easily reveals the Tafel overpotential component η'_2 , when the system is in quasi-equilibrium state (electrochemical current equal zero). In our case, after the H loading and its stabilization in the cathode via chemical procedure, the polarization is switched off and the system sets off to equilibrium exhibiting an overpotential η'_2 . Considering the Nernst equation that relates the chemical potential

to fugacity, in our experimental loading a $\eta_2 \approx 900(500)$ mV stable value is achieved, corresponding to an equivalent pressure of 10^{30} (10^{17}) atmosphere.

Fifth point of the Baranowski/Dębowska letter [1] the following comment is given "... if such overstoichiometric high concentrated samples are really interesting from the point of view of superconductivity? Rather discouraging are in this respect the results of hydrogen concentration increase realized by implantation technique, whereby locally H:Pd ratios of 1.2 were achieved..."

It is well known that the hydrogen in Pd samples at high x value ($x \sim 1$) is very unstable. Moreover, H is moving inside lattice at temperature of about 100 K [16], so that during various thermal cycles (300–4.2 K) the PdH samples may have a slight H de-loading. Hence the measured T_c rarely corresponds to the measured x value during the H loading process. We have bestowed on the H stability for high x value in PdH samples much attention and many experimental experiences based on electrochemical approach explained in our paper [5]. Our PdH samples are stable and only if the mean x value in PdH sample is well stable, it is possible to have a "true" correspondence between T_c and x parameter.

Sixth point of the Baranowski/Dębowska letter [1] comments: "... It is known, that in the temperature range 1.5–9 K the critical temperature is a linear function of hydrogen activity.... An extrapolation to 298 K gives the logarithm of hydrogen fugacity equal to about 160, thus a pressure not accessible in experiments...".

These sentences [17,18] just as predictions based on our phenomenological model [4] are extrapolations in a very wide range of variables in respect to the measurements and as such, useful only as a possible indication and not as a predictable value of real experimental results.

In conclusion, let us not forget that the scientific debate is based on, and due to, significant experimental discoveries. In fact, the HTSC ceramic superconductors, after the Meissner signal measurements, have been accepted as superconductors but why they are superconductors is still a debate matter, whereas a significant step towards the understanding of the HTSC in PdH_x system functioning has been done. Ashcroft's publication [19] provides evidence that H dominant metal alloy may exhibit high temperature superconductivity over a modest external pressure range. The advantage of saturated hydrides in terms of achieving HTSC is, that chemically, high H compression inside the hosting metal lattice is already

formed and hence the metallic H phase where the electrons from both hydrogen and host metal may participate in common overlapping bands.

We have reported, as invited talk [7], the ZFC/FC susceptibility measurements (Meissner effect) of our PdH sample at the Sixth International Conference on new theories, discoveries, and applications of superconductors and related materials on 9–11 January in Sydney, Australia. The data in the figure that gives a sign of weak superconductivity indicates that some fraction of superconducting sample with $T_c \approx 235$ K is distributed within the non-HTSC sample or within the superconducting sample with lower transition temperature. In other words, there is the presence of randomly distributed Josephson junctions [20] between the HTSC regions with $T_c \approx 235$ K. These small regions could be hyper-stoichiometric PdH₂ sub-structure at the grain boundary with $T_c \gg 235$ K and superconducting PdH_x matrix with $x \approx 1$ and $T_c \ll 235$ K.

In order to express an objective consideration on PdH superconductivity work, we do kindly invite the colleagues, to take into consideration all the literature in the field, including and especially the latest publications.

References

- [1] B. Baranowski, L. Dębowska, J. Alloys Compd. 437 (2007) L4–L5.
- [2] P. Tripodi, M.C.H. McKubre, F.L. Tanzella, et al., Phys. Lett. A 276 (2000) 122–126.
- [3] P. Tripodi, D. Di Gioacchino, R. Borelli, J.D. Vinko, Physica C 389 (2003) 571.
- [4] P. Tripodi, D. Di Gioacchino, J.D. Vinko, Physica C 408–410 (2004) 350–352.
- [5] P. Tripodi, D. Di Gioacchino, J.D. Vinko, Bras. J. Phys. 34 (2004) 1177.
- [6] P. Tripodi, D. Di Gioacchino, J.D. Vinko, J. Phys. Conf. Ser. 43 (2006) 690–693.
- [7] P. Tripodi, D. Di Gioacchino, J.D. Vinko, Int. J. Mod. Phys. B 21 (2007) 3343–3347.
- [8] R.A. Hein, T.L. Francavilla, D. Liebenberg, Magnetic Susceptibility of Superconductors and Other Spin Systems, Plenum Press, 1991, pp. 84–85.
- [9] C. Poole Jr., H.A. Farach, R.J. Creswick, Superconductivity, Academic Press, 1995.
- [10] A. Lipson, B.J. Heuser, C. Castano, G. Miley, B. Lyakhov, A. Mitin, Phys. Rev. B 72 (2005) 212507.
- [11] A. Lipson, B.J. Heuser, C. Castano, A. Celik-Aktas, Phys. Lett. A 339 (2005) 414–423.
- [12] A. Lipson, B.J. Heuser, C. Castano, et al., J. Exp. Theor. Phys. 103 (2006) 385–397.
- [13] R.A. Oriani, The Physical and Metallurgical Aspects of Hydrogen in Metals, ICCF4, Lahaina, Maui, 1993.
- [14] J. O'M Bockris, A.K.N. Reddy, M. Gamboa-Adelco, Modern Electrochem. 2A, Springer 2nd Edition (2001).
- [15] M. Enyo, J. Electroanal. Chem. 134 (1982) 75–86.
- [16] H. Hemmes, A. Driessens, R. Griessens, Phys. Rev. B 39 (1989) 212507.
- [17] B. Baranowski, L. Dębowska, Polish. J. Chem. 80 (2006) 843.
- [18] M. Tkacz, B. Baranowski, Roczn. Chem. 50 (1976) 2159.
- [19] N.W. Ashcroft, Phys. Rev. Lett. 92 (2004) 187002.
- [20] P.M. Grant, S.S. Parkin, V.Y. Lee, et al., Phys. Rev. Lett. 58 (1987) 2482.