

Pd-H system as a possible room temperature superconductor

Paolo Tripodi ^{a,1}, Daniele Di Gioacchino ^b, Jenny Darja Vinko ^c

^a*E.N.E.A.- Centro Ricerche Frascati, via Enrico Fermi 45, 00044 Frascati, Italy*

^b*I.N.F.N., Frascati National Laboratory, via Enrico Fermi 40, 00044 Frascati, Italy*

^c*H.E.R.A. S.r.l. Hydrogen Energy Research Agency, Corso della Repubblica 448, 00049 Velletri, Italy*

Abstract

Some experimental data on PdH(D) at 300K, shows resistivity (ρ) less than the pure Pd. Moreover T_c greater than 9K reported in literature has been measured, hence a phenomenological description of the ρ for highly loaded PdH(D) system at 300K has been developed. This approach uses a parallel model of two concurrent electrical transport processes: i) ρ has a linear raise with the concentration $x = \text{H/Pd}$, due to the increase of Pd relative lattice volume ii) ρ has an exponential decrease versus x due to superconducting fluctuations at very high x in PdH(D). Superconducting state appears at $x_c(300\text{K})$. Inverse isotopic effect for $0.6 \leq x \leq 0.96$ changes to normal isotopic effect at $x \approx 1$.

Key words:

PdH(D); HTSC; room temperature superconductor

1. Introduction

Relative resistance R/R_0 of the PdH_x versus stoichiometry x , where R_0 is the resistance of pure Pd, is usually interpreted with the Mott and the modified Mott model for metals and metal-alloys [1]. This model considers two phases: α -phase ($0 \leq x \leq 0.02$), β -phase ($x \geq 0.6$) and their coexistence $[\alpha + \beta]$ -phase ($0.02 \leq x \leq 0.6$) in Pd, but it is not able to explain the experimental R/R_0 values less than unit at 300K [2][3], at 100K [4] and T_c in stable PdH_x ($x \geq 1$) samples [5] much higher than 9K previously measured [6], therefore a new phenomenological approach to explain the Pd-H(D) electrical resistance behaviors for $x \geq 1$ at 300K will be proposed. The Pd-H(D) resistance consists of two different electric transport mechanisms. Increasing x , the first correlates the R/R_0 increasing with the lattice structure change during the Octahedral (O) sites filling up and the second describes the exponential decreasing of R/R_0 .

2. Discussion

In the first mechanism the increasing of x affects the interaction between the H and Pd lattice with consequent increasing of the electron-phonon scattering. Moreover the slow motion (acoustic phonon) of Pd lattice is very sensitive to the H^+ fast hopping motion between O-sites [7]. The increasing of R/R_0 vs x can be correlated with the linear lattice expansion in Pd-H(D) for $0 \leq x \leq x_0$ where x_0 is the stoichiometric value when R/R_0 has the maximum value. We describe R/R_0 linear change in the first eq.1 where the parameter m is directly correlated with the increasing of Pd relative volume. For the second mechanism the following evidences must be considered.

The electronic configuration changes due to the filling up of the d-band vacancies, hence a reduction of s-d scattering and R/R_0 would be expected [3][8]. H vibration around their O-sites at very high frequencies (optical phonon) probably affect the normal resistance [9]. Because of the diffusion of H, these optical modes are local and independent from the Pd lattice vibrations [7]. Increasing x , the density of H in the O-

¹ E-mail: paolo.tripodi@frascati.enea.it

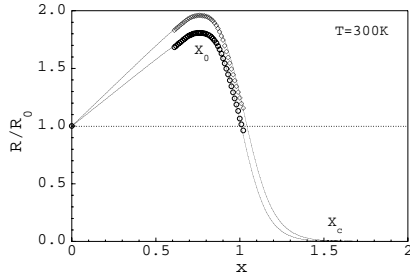


Fig. 1. R/R_0 fit of experimental data for PdH and PdD vs x

sites increases and these optical modes should become non local. These optical modes are correlated with the superconductivity in the Pd-H(D,T) systems [9].

Moreover, the following data should be considered: i) unexplained experimental evidences ($R/R_0 \leq 1$) at 300K; ii) susceptibility measurements show a paramagnetic-diamagnetic transition above $x=0.7$ [10]; iii) well known superconducting transition at low temperature and high x [6]. iv) $T_c \geq 9K$ for stable samples with $x \geq 1$ [5].

A fluctuation process of the superconducting state that is responsible for Pd-H(D) electrical resistance decrease ($x \geq x_0$) is suggested and consequently condensation of macroscopic superconducting state occurs at $x = x_c$ [11]. These processes are described:

$$\left(\frac{R}{R_0}\right)_{lin} = 1 + mx \quad ; \quad \left(\frac{R}{R_0}\right)_{exp} = \beta e^{-\gamma(x-x_0)} \quad (1)$$

the second eq.1 considers the thermodynamic fluctuation of the superconducting state:

$$\gamma(x-x_0) = \frac{U}{KT} \quad ; \quad U = \left(\frac{H_c^2(T)\xi^3(T)}{8\pi}\right) \cdot n \quad (2)$$

where U is the free-energy increment [11] or the condensation energy of the superconducting domains around T_c , n is the number of domains at fixed concentration x in $x_0 \leq x \leq x_c$. Using equations (2):

$$\gamma(T) = \frac{H_c^2(T)\xi^3(T)}{KT} \quad ; \quad n = (x - x_0) \quad (3)$$

the prefactor β [11] is correlated to the frequency described in the fluctuation theory. The value $x=x_c$, where R/R_0 is zero, is the end of the thermodynamic fluctuations and the Pd-H(D,T) system is in a macroscopic superconducting state. Hence, the U value calculated at x_c is the condensation energy of the macroscopic superconducting state. The fit of the experimental R/R_0 data are shown in fig.1 and the T_c vs x_c is shown in fig.2.

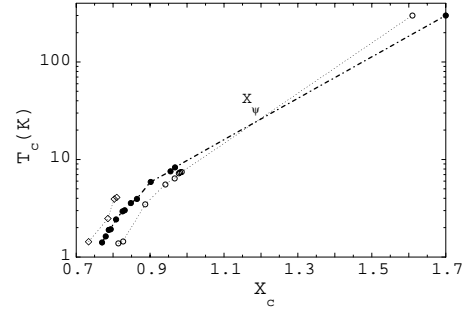


Fig. 2. T_c versus x_c for H (\circ), D (\bullet) and T (\diamond) experimental data plotted with the theoretical results

3. Conclusion

Results of the proposed phenomenological theory that consider the simultaneity of two processes as the parallel between the two R/R_0 (linear and exponential) are:

- i) $T_c=300K$ for $\gamma_H=12.4$, $\gamma_D=11.2$, $x_c(H)=1.6$, $x_c(D)=1.7$. The condensation energy of the superconducting states is $U_H=270meV$ and $U_D=273meV$
- ii) $x_c(D) \geq x_c(H)$ for $T_c(D)=T_c(H)=300K$ shows a normal isotopic behavior ($T_c(D) \leq T_c(H)$) (fig.2);
- iii) x_ψ where $T_c(D)=T_c(H)$ is the threshold point from the inverse ($T_c(D) \geq T_c(H)$) to normal ($T_c(D) \leq T_c(H)$) isotopic behavior;

There is a correlation between condensation energy values and experimental data [12] on potential barrier between O-sites and T-sites in PdH. Probably to achieve high T_c in highly loaded PdH(D) system the occupation of T-sites is important.

References

- [1] N.F. Mott H.Jones, The theory and properties of metals and alloys, Dover Pub. Inc. NY (1958) 296
- [2] S. Crouch-Baker et al, Z.fur Phys. Chemie.**204** (1998) 247
- [3] G. Bambakivis et al, Phys. Rev.**177** (1969) 1044
- [4] H. Hemmes et al, Phys. Rev.**B39** (1989) 4110
- [5] P. Tripodi patent WO0167525
- [6] T.Skoskiewicz et al, Solid State Phys.**7** (1974) 2670
- [7] M. H. Lee, Separation Sci. and Tech. , **15** (1980) 457
- [8] B.M.Geerken et al, J. Phys. F: Met. Phys.**13** (1983) 963
- [9] D.S. MacLachlan et al, Sol. Stat. Comm.**17** (1975) 281
- [10] F.A.Lewis, The Palladium Hydrogen System, Academic. Press (1967) 148
- [11] M.Thinkam, Introduction to superconductivity , McGraw-Hill (1975) 234
- [12] C. Elsasser, K.M.Ho et al, Phys.Rev.B **44** (1991) 10377