



# **SUPERCONDUCTIVITY IN ISOELECTRONIC ALLOYS OF PdH<sub>x</sub>**

S. Bredenkamp, D. Mclachlan, J. Burger

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SUPERCONDUCTIVITY IN ISOELECTRONIC ALLOYS OF  $\text{PdH}_x$ S.H. Bredenkamp, D.S. McLachlan and J.P. Burger<sup>+</sup>

<sup>+</sup> University of the Witwatersrand, Johannesburg, South Africa  
 Laboratoire de Physique des Solides, Orsay 91405, France

Résumé.- Nous mesurons la température de transition supraconductrice  $T_c$  d'alliage  $\text{Pd}_{0.91}\text{Ag}_{0.045}\text{Rh}_{0.045}\text{H}_x$  avec  $x \lesssim 1$ . Ces  $T_c$  sont diminuées de moitié par rapport à  $\text{PdH}_x$ , un effet que nous attribuons à des changements dans le spectre des phonons optiques.

Abstract.- The superconducting transition temperatures ( $T_c$ ) of  $\text{Pd}_{0.91}\text{Ag}_{0.045}\text{Rh}_{0.045}\text{H}_x$  are measured for  $x \lesssim 1$ . The observed  $T_c$ 's are about one half those of  $\text{PdH}_x$   $\lesssim 1$ . This is attributed to changes in the optical phonon spectrum.

It has recently been found<sup>1,2/</sup> that Pd-noble metal alloy hydrides such as  $\text{Pd}_{1-y}\text{Ag}_y\text{H}_x$  can have transition temperatures as high as 17 K. When the noble metal is silver the maximum transition temperature of the  $\text{Pd}_{(1-y)}\text{Ag}_y\text{H}_x$  initially rises<sup>3/</sup> at a rate of 0.45 K per % Ag. If rhodium replaces the silver, the maximum transition temperature of the  $\text{Pd}_{(1-y)}\text{Rh}_y\text{H}_x$  is found<sup>3/</sup> to decrease at the same rate, i.e. 0.45 K per % Rh. This symmetry suggested that a study of the alloy  $\text{Pd}_{1-2y}\text{Ag}_y\text{Rh}_y\text{H}_x$  would be interesting as these alloys, which are isoelectronic to  $\text{PdH}_x$ , should have not only similar electronic properties but also similar ionic properties due to the small mass differences between Rh, Pd and Ag.

As the amount of Ag and Rh which, in equal quantities, will form a solid state solution in Pd is unknown<sup>4/</sup>, a relatively dilute alloy ( $\text{Pd}_{0.91}\text{Ag}_{0.045}\text{Rh}_{0.045}$  by atomic absorption analysis) was prepared. The alloy was then rolled to a thickness of approximately 60 microns before being given the heat treatments shown in table I. A subsequent X-ray analysis of the "as rolled" samples showed the very blurred and smudged rings characteristic of a rolled material while the annealed samples showed sharp rings which could not be distinguished from those of pure Pd. This X-ray study and the fact that the width of the superconducting transition temperature is narrower for the annealed samples leads us to believe that  $\text{Pd}_{0.91}\text{Ag}_{0.045}\text{Rh}_{0.045}$  is a homogeneous single phase alloy. The foils were hydrogenated at  $-78^\circ\text{C}$ , using the electrolysis method described in reference<sup>5/</sup>.

The hydrogen content (see table I) was obtained from both the resistivity and outgassing in a constant volume apparatus. The outgassing method

Table I

Note : Samples 4a and b as well as 5a and b are the same pieces of foil which have been hydrogenated twice. Sample 1 is a pure Pd foil done for control.

Sample Number	Heat Treatment	$T_c$	Width	Hydrogen Concentration from	
				Resistivity	Outgassing
1 (Pd)	as rolled	9.43	.43	.995	Not done
2	as rolled	2.90	1.8	.978	.973
3	as rolled	2.60	1.7	.961	
4a	16 hrs at $850^\circ\text{C}$	2.1	.72	.963	.972
4b	$850^\circ\text{C}$	3.93	.80	.995	1.05
5a	16 hrs at $850^\circ\text{C}$	3.49	.51	.979	-
5b	plus 1 1/2 hrs at $1000^\circ\text{C}$	3.36	.63	.962	.970

proved less accurate and subject to accidents (samples 3 and 5a). The resistivity method is inherently better for measuring small changes in X at high concentrations, because it depends on the relatively large change in the hydrogen vacancy concentration. The basic assumption in determining the hydrogen content from the resistivity was that, as in  $\text{PdH}_x$ , the hydrogen vacancies contribute  $0.85 \mu\Omega\text{cm}$  per % H vacancies to the residual resistivity<sup>6/</sup>. We have confidence in our X results as the two methods differ by only slightly more than 1 %.

After hydrogenation the samples (while under liquid nitrogen); were cut, stored and placed in the secondary coil of a mutual inductance. After being rapidly transferred to the helium cryostat the change in signal, from the mutual inductance, was measured as a function of temperature. The temperature

was controlled electronically and measured using a germanium thermometer.

Listed in table I are the transition temperatures and transition temperature widths of all the samples. The transition temperature is the temperature at which the signal from the mutual inductance has changed by 50 % of the total change and the width is the temperature difference between the points where the signal has changed by 90 % and 10 %. In figure 1 these transition temperatures and transition temperature widths are plotted as a function of the total residual resistivity and as a function of the hydrogen concentration deduced from this residual resistivity.

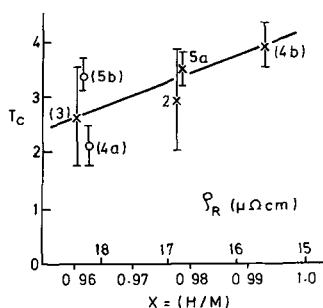


Fig. 1 :  $T_c$  and transition width as a function of residual resistivity  $\rho_R$  and as a function of hydrogen concentrations.

The line through these results is the extrapolation to  $X = 1$ . This extrapolation gives  $T_c$  for  $\text{Pd}_{0.91}\text{Ag}_{0.045}\text{Rh}_{0.045}\text{H}$  as 4.1 K, which is a factor of at least two below  $T_c$  for  $\text{PdH}/6,7,8/$ . The slope of the line, about 0.4 K per % hydrogen, is lower than the value of about 0.63 per % hydrogen observed by Miller and Satterthwaite/7/ in the range  $X = 0.95$  to 1 and is considerably lower than the value of about 1 K per % H observed by McLachlan et al./8/ in the range  $X = 0.98$  to 1.

Due to a complete lack of information on any other properties of the alloy and hydrides of the alloy the discussion will be limited to qualitative arguments. The BCS formula for  $T_c$  can be written in the form

$$T_c = \theta_D e^{-1/\lambda_{\text{eff}}} = \left(\frac{\hbar}{k}\right)^{1/2} \frac{f}{M} \exp - \frac{f}{N(0)I^2}$$

where  $\theta_D$  is the Debye (Einstein) temperature of,  $f$  the mean force constant for and  $M$  the mean ionic mass for either the acoustic or the optical phonon band.  $N(0)I^2$  is the electronic factor of the alloy.

Due to the nature of the alloy it is hard to see the factors  $M$ ,  $N(0)I^2$  or  $f_{\text{ac}}$  varying significantly from those for  $\text{PdH}$ . However, theoretical calculations/9, 10/ and experimental results/6/ have shown that the electron-optic phonon interaction is about three times larger than the electron-acoustic phonon interaction in  $\text{PdH}_{x \approx 1}$ . It is therefore most likely that the change in  $T_c$  is due to a shift in  $f_{\text{op}}$ , which is essentially the force constant for the hydrogen ions in the octohedral vacancies. Taking the characteristic temperature of the optic phonons in  $\text{PdH}$  as 600 K/6/, a change in  $f_{\text{op}}$  of only 22 % is necessary to account for the shift in  $T_c$ .

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