

# Superconductivity of solid hydrogen solutions in palladium alloys with noble metals

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The behavior of transition temperature to the superconducting state for hydrogen solutions with a fcc sublattice of the metal based on  $\text{Pd}_{60}\text{Cu}_{40}$  and  $\text{Pd}_{80}\text{Ag}_{20}$  alloys at  $T > 2$  K is investigated. The alloys were saturated with hydrogen at  $P_{\text{H}_2} < 70$  kbar.

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Superconductivity appears in the Pd-H system when the atomic ratio for hydrogen/metal is  $n \geq 0.8$ .<sup>1</sup> As shown in a number of studies, a further increase of hydrogen content increases monotonically the transition temperature to the superconducting state to  $T_c \approx 8.8$  K at  $n = 1$ , see review article.<sup>2</sup> Even higher  $T_c$  of the order of 13–17 K were reached by implanting hydrogen into palladium alloys with noble metals—copper, silver, and gold.<sup>3</sup> The  $T_c(n)$  curves for each of these alloys have a maximum, and the dependences of these maximum values of  $T_c$  on the content of the noble metal in palladium in turn also go through the maximum. For example, in the Pd-Cu-H system the optimum value of  $T_c = 16.6$  K was obtained in the  $\text{Pd}_{55}\text{Cu}_{45}$  alloy (atomic percents) at  $n \sim 0.7$ , and in the Pd-Ag-H system  $T_c = 15.6$  K was obtained in the  $\text{Pd}_{70}\text{Ag}_{30}$  alloy at  $n \sim 0.8$ .<sup>3</sup>

Stritzker's<sup>3</sup> results produced a large interest and were discussed many times in the literature (see Ref. 2) and during conferences. The data,<sup>3</sup> however, were obtained by using rather unique samples: the hydrogen, contained only in a narrow layer  $\sim 1500$  Å, was distributed nonuniformly along its thickness; the metal lattice in this layer was intentionally damaged during the implantation, etc. Of interest was the study of the  $T_c(n)$  dependences in the massive, homogeneous samples saturated with hydrogen under conditions close to the equilibrium, to which this work is devoted.

We selected  $\text{Pd}_{60}\text{Cu}_{40}$  and  $\text{Pd}_{80}\text{Ag}_{20}$  alloys for investigation, i.e., close to optimum compositions. The ingots were melted out of electrolytic Pd, Cu, and Ag in an induction furnace in a vacuum. After homogenizing at  $T = 1200$  K for 6 h in a vacuum and quenching in water, the ingots were rolled into 0.2-mm-thick strips, again annealed at 122 K for 5 min in a vacuum to eliminate mechanical stress and quenched in water. The samples cut out of these strips were hydrogenated at  $P_{\text{H}_2} < 70$  kbar and at  $T = 520$  K for 8 h and then quenched at a pressure up to  $\sim 150$  K (at  $P = 1$  atm a noticeable liberation of hydrogen from the samples began at  $T \geq 220$  K). The  $\text{Pd}_{60}\text{Cu}_{40}$  (Ref. 4) and  $\text{Pd}_{80}\text{Ag}_{20}$  (Ref. 5) alloys produce with hydrogen broad regions of solid interstitial solutions based on a fcc metal sublattice and, in particular, the Me-H samples investigated in this work must be single-phase.

The hydrogen content in the alloys was determined with an accuracy of  $\delta n \sim 0.05$  by decomposing them into metal and molecular hydrogen in a closed container of known volume that was preliminarily evacuated to a pressure of  $10^{-2}$  atm.

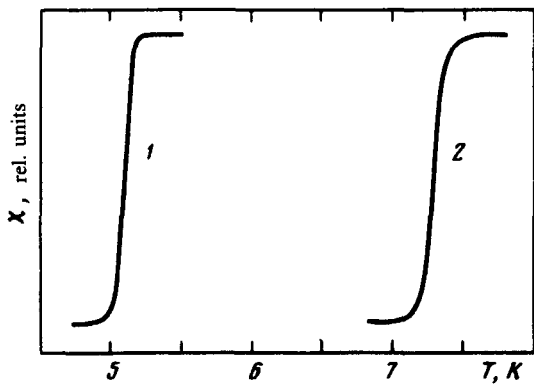


FIG. 1. Temperature dependences of the magnetic susceptibility  $\chi(T)$  of  $\text{Pd}_{80}\text{Ag}_{20}\text{-H}$  sample at  $n = 0.97$  (1) and 1.00 (2).

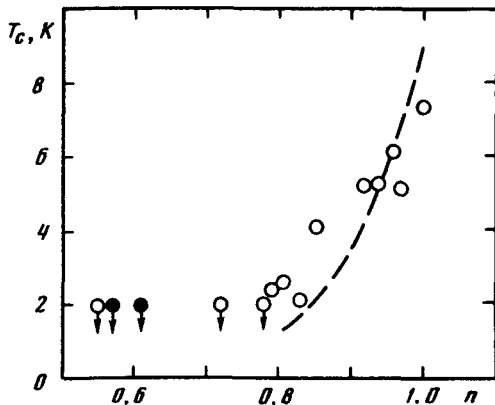


FIG. 2. Dependence of the temperature  $T_c$  of transition to the superconducting state on the hydrogen-metal atomic ratio  $n$ :  $\circ$ , for  $\text{Pd}_{80}\text{Ag}_{20}\text{-H}$  solution and  $\bullet$ , for  $\text{Pd}_{60}\text{Cu}_{40}\text{-H}$  solution. The symbols with arrows show that superconductivity is missing in these samples at  $T > 2$  K. The dashed line represents the  $T_c(n)$  dependence for the Pd-H solutions.<sup>2</sup>

In  $\text{Pd}_{80}\text{Ag}_{20}\text{-H}$  solutions  $T_c$  increases above 2 K at  $n \gtrsim 0.8$ . Typical curves for the temperature dependence of the signal, which is proportional to the magnetic susceptibility  $\chi$  of the sample, are shown in Fig. 1. A small width of the susceptibility jumps ( $\leq 0.15$  K), corresponding to the transition to the superconducting state, indicates that the distribution of hydrogen in the sample is uniform. The values of  $T_c$  for  $\text{Pd}_{80}\text{Ag}_{20}\text{-H}$  solutions, which were determined from the locations of the midpoint of the jumps on the  $\chi(T)$  dependences, are shown in Fig. 2. It can be seen that the  $T_c(n)$  dependence for these solutions is close to that for the Pd-H solutions (dashed line in Fig. 2). We recall that for  $\text{Pd}_{80}\text{Ag}_{20}\text{-H}$  solutions obtained by hydrogen implantation  $T_c$  reached  $\sim 15$  K already at  $n \sim 0.8$ .<sup>3</sup>

The maximum hydrogen content in the  $\text{Pd}_{60}\text{Cu}_{40}\text{-H}$  samples obtained in this

work was  $n = 0.61 \pm 0.05$ . As seen in Fig. 2, dissolution of such amount of hydrogen did not produce superconductivity at  $T \geq 2$  K, also inconsistent with Stritzker's data.<sup>3</sup>

Thus, the results of this work show that the high values of  $T_c$  of the solutions in the palladium alloys with noble metals, which were observed in Ref. 3, are attributable to the specific properties of the metastable state of the thin hydrogenous layer obtained during hydrogen implantation at a low temperature. It is most probable that, like in many other systems obtained by implantation,<sup>2</sup> an increase of  $T_c$  is due to large imperfections in the crystal lattice of a metal-target.

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