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Superconductivity and Atomic Ordering  
of Pd-Cu-H Solid Solutions

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Due to a number of nontrivial physical properties, hydrogen solutions in the palladium alloys with noble metals (Cu, Ag, and Au) have attracted the researchers attention for many decades /1, 2/. The beginning of the latest and, perhaps, most intensive outburst of interest in these systems can be dated 1974 when the solutions charged with hydrogen by implantation were found to possess superconducting temperatures,  $T_K$ , up to 13 to 17 K that considerably exceeded a maximum attainable value of  $T_K \approx 9$  K for the Pd-H solutions /3/. Unexpected phenomena, however, did not end here, and further experiments have shown the effects observed in /3/ to be due to specific peculiarities of thin hydrogen-containing layers forming in the process of implantation since superconducting properties of massive homogeneous samples of the Pd-noble metal-H solutions proved to be quite different. In particular, having been synthesized under high hydrogen pressure, the  $\text{Pd}_{97}\text{Au}_3\text{-H}$ ,  $\text{Pd}_{91}\text{Au}_9\text{-H}$  /4/, and  $\text{Pd}_{80}\text{Ag}_{20}\text{-H}$  /5/ samples exhibited dependences of  $T_K$  upon the H-to-metal atomic ratio  $n$  which were close to the  $T_K(n)$  dependence for the Pd-H solutions, and the  $\text{Pd}_{60}\text{Cu}_{40}\text{-H}$  samples with  $n \lesssim 0.6$  possessed no superconductivity at  $T \cong 2$  K /5/. But these findings, too, still did not exhaust the results, and at high hydrogen pressure and elevated ( $\cong 150$  to  $250^\circ\text{C}$ ) temperatures new phase transformations accompanied by atomic ordering of metal sublattices of solid solutions have been revealed in the  $\text{Pd}_{50}\text{Ag}_{50}\text{-H}$  /6/ and  $\text{Pd}_{60}\text{Cu}_{40}\text{-H}$  /7/ systems. An X-ray examination of a single-crystal specimen allowed to draw the conclusions /8/ that at  $P_{\text{H}_2} = 1.1$  GPa and  $T = 300^\circ\text{C}$  the ordering of metal atoms in the  $\text{Pd}_{60}\text{Cu}_{40}\text{-H}_2$  solution is of the  $\text{CuAuI} (\text{Ll}_o)$  type.

The present work is undertaken in order to study the  $T_K(n)$  dependences for both disordered and ordered Pd-Cu-H solutions. The alloys with 10, 20, 25,

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30, 35, and 40 at% Cu are under study. The ingots were melted in an induction furnace in vacuum from electrolytical Pd and Cu. After a 6 h homogenization in vacuum at 930 °C and water quenching these ingots were rolled into strips 0.15 mm thick, then subjected to stress-relief annealing in vacuum at 930 °C for 5 min and again quenched in water. The specimens in the form of discs of 4 mm diameter were cut out of these polycrystalline strips.

Hydrogenation of the samples was conducted by a 24 h exposure in hydrogen atmosphere at fixed magnitudes of temperature ( $100 \leq T \leq 300$  °C) and pressure ( $P_{H_2} \leq 8$  GPa); the technique for compressing hydrogen is described in /9/. The temperature and the pressure were measured with an accuracy to  $\pm 10$  °C and  $\pm 0.3$  GPa, respectively. After the hydrogenation was completed, the high-pressure chamber was rapidly cooled down to  $\approx -180$  °C (this temperature was low enough to prevent hydrogen losses from the Pd-Cu-H samples after subsequent lowering the pressure down to atmospheric), then the pressure was lowered and the samples were taken out of the chamber and later on kept in liquid nitrogen. The hydrogen content of the samples was measured to an accuracy of 5%; a detailed description of the technique is given in /7/. An X-ray study was carried out by a phototechnique at  $T = -190$  °C using a DRON-2.0 diffractometer with  $CuK_{\alpha}$  radiation. The  $T_K$  values were determined by the induction method at  $T \geq 2$  K.

Under normal conditions and a copper content up to  $\approx 45$  at%, palladium and copper form continuous disordered solid solutions with the f.c.c. lattice /10/. According to /11, 12/, the copper alloying of palladium results in a monotonic decrease in the critical temperature of the separation of the Pd-H solutions into the two isomorphous phases, poor and rich in hydrogen, down to room temperature for the alloy with  $\approx 35$  at% Cu, and, thus, in the range of high hydrogen concentrations, interesting for our purposes, the Pd-Cu-H samples under study should be single-phase hydrogen interstitial solutions on the basis of the starting disordered f.c.c. lattice of the Pd-Cu alloys (hereinafter referred to as the  $\gamma$ -solutions).

The X-ray study has shown that actually only  $\gamma$ -solutions form in the  $Pd_{90}Cu_{10}$ -H system (as well as in the Pd-H system) in the temperature and pressure range investigated in the present work, whereas at  $T \gtrsim 150$  °C the solutions on the base of the alloys with  $\geq 20$ at% Cu undergo an irreversible

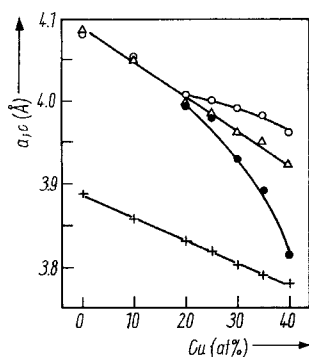


Fig. 1. Parameters of the metal lattice at  $-190^{\circ}\text{C}$  and atmospheric pressure for the initial Pd-Cu alloys (+) and for the Pd-Cu-H samples obtained by 24 h exposure at  $P_{\text{H}_2} = 2 \text{ GPa}$  and  $100^{\circ}\text{C}$  ( $\Delta$ );

$300^{\circ}\text{C}$  ( $\circ$ ,  $\bullet$ ) (the hydrogen content of the samples was (at% Cu-n at  $100^{\circ}\text{C}$ /n at  $300^{\circ}\text{C}$ ): 0-0.99/0.98; 10-0.94/0.92; 20-0.81/0.81; 25-0.71/0.78; 30-0.69/0.72; 35-0.70/0.72; 40-0.57/0.55). For the  $\gamma$ -samples parameters  $a$  of the f.c.c. cell (+,  $\Delta$ ,  $\circ$ ) are shown; for the  $\gamma'$ -samples parameters  $a$  ( $\circ$ ) and  $c$  ( $\bullet$ ) of the f.c.t. quasi-cell are given

phase transition followed by tetragonal distortions of their metal lattices, i.e. ordered solutions are formed (henceforth  $\gamma'$ -solutions). To illustrate the observed effects, the X-ray data for the  $\gamma$ - and  $\gamma'$ -samples obtained at  $P_{\text{H}_2} = 2 \text{ GPa}$  are presented in Fig. 1. It should be noted that while the X-ray photographs of the  $\text{Pd}_{60}\text{Cu}_{40}\text{-H}$   $\gamma'$ -samples contained a considerable number of superstructural lines in addition to the basic ones of the f.c.t. lattice (see /7/), only one (the strongest) of the superstructural lines, (110), could be seen in the photographs of the  $\text{Pd}_{65}\text{Cu}_{35}\text{-H}$   $\gamma'$ -samples, and even the basic lines, including those of  $\{111\}$  type which do not split at tetragonal distortions of the lattice, were significantly broadened in the photographs of the  $\gamma'$ -samples with still lower copper concentration. The broadening of the diffraction lines along with the decrease in the degree of the lattice tetragonality (Fig. 1) with decrease of the copper content of the Pd-Cu-H  $\gamma'$ -samples is in accordance with the conclusion /8/ that the ordering of the metal atoms in the Pd-Cu-H solutions conforms to the PdCu stoichiometry. Considerable broadening of the  $\{111\}$ -type lines for the  $\gamma'$ -samples on the base of the alloys with 20, 25, and 30 at% Cu is indicative of their concentration inhomogeneity arising in the process of the ordering.

A noticeable broadening of all the lines was also observed in the X-ray photographs of the  $\gamma$ -samples on the base of these alloys obtained by exposure under high hydrogen pressure and  $T = 100^{\circ}\text{C}$ , the linewidths increasing when the interval of the exposure increased from 24 to 72 h. This broadening was apparently due to a concentration inhomogeneity of the samples arising at initial stages of the ordering process (at high hydrogen pressure and  $T = 100^{\circ}\text{C}$  the

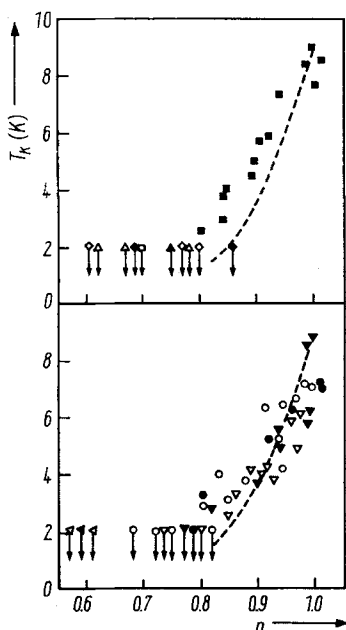


Fig. 2. Dependences of superconducting transition temperature,  $T_K$ , on the H-to-metal atomic ratio,  $n$ , for the Pd-Cu alloys with  $\blacktriangleright$  0;  $\blacksquare$ ,  $\square$  10;  $\bullet$ ,  $\circ$  20;  $\blacktriangledown$ ,  $\triangledown$  25;  $\blacklozenge$ ,  $\lozenge$  30;  $\blacktriangle$ ,  $\triangle$  35;  $\blacktriangleleft$ ,  $\triangleleft$  40 at% Cu. Closed symbols pertain to the  $\gamma$ -samples, open ones pertain to the  $\gamma'$ -samples. Symbols with arrows stand for the samples possessing no superconductivity at  $T \approx 2$  K. Dashed line represents the  $T_K(n)$  dependence for the Pd-H solutions /15/

thermodynamical equilibrium state of the samples was obviously the ordered one, which did not realize owing to just kinetical reasons /7/).

Characterizing the studied samples taken as a whole, it is worth noting that the increment of the volume of the Pd-Cu-H solutions (both  $\gamma$ - and  $\gamma'$ -ones) with the hydrogen concentration was in good agreement with the "universal" dependence suggested in /13/ to describe the data for a great number of hydrogen  $\gamma$ -solutions in various palladium alloys (this dependence, corrected in the concentration interval  $0.7 \lesssim n \lesssim 1$  using the most reliable data of /14/ for Pd-H solutions, is given in /4/). The magnitudes of  $c/a$  ratio for the  $\gamma'$ -samples varied depending upon treatment conditions under high hydrogen pressure within the limits 0.995 to 0.985 for the alloys with 20 and 25 at% Cu; 0.995 to 0.97 - with 30 and 35 at% Cu; 0.97 to 0.94 - with 40 at% Cu.

The data of the measurements on the  $T_K(n)$  dependences for the Pd-Cu-H solutions are presented in Fig. 2. As is seen from the figure, at the attained hydrogen concentrations both the  $\gamma$ - and  $\gamma'$ -samples based on the alloys with 40, 35, and 30 at% Cu possessed no superconductivity at  $T \approx 2$  K. Typical dependences  $\Delta(T)$  of the signal of disbalance of an ac bridge in the range of transition to the superconducting state for the  $\text{Pd}_{75}\text{Cu}_{25}$ -H and  $\text{Pd}_{90}\text{Cu}_{10}$ -H samples are demonstrated in Fig. 3. The large width of the steps of the  $\Delta(T)$  dependences for the  $\text{Pd}_{75}\text{Cu}_{25}$ -H solutions is likely due to their concentration

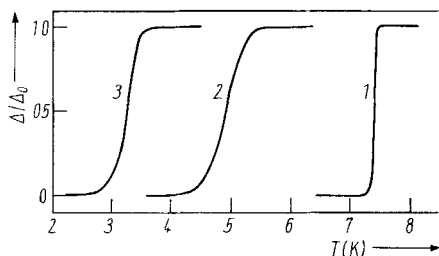


Fig. 3. Temperature dependences of the signal of disbalance  $\Delta$  of an ac bridge in the range of transition to the superconducting state for (1)  $\text{Pd}_{90}\text{Cu}_{10}\text{-H}$   $\gamma$ -sample,  $n = 0.94$ ; (2)  $\text{Pd}_{75}\text{Cu}_{25}\text{-H}$   $\gamma$ -sample,  $n = 0.94$ ; (3)  $\text{Pd}_{75}\text{Cu}_{25}\text{-H}$   $\gamma'$ -sample,  $n = 0.86$ .  $\Delta_0$  is the magnitude of the signal for samples in the normal state

inhomogeneity mentioned above (the  $\Delta(T)$  dependences for the  $\text{Pd}_{80}\text{Cu}_{20}\text{-H}$  samples were of similar character). The  $T_K$  values presented in Fig. 2 were estimated from the step midpoint locations. One can see from Fig. 2 that the  $T_K(n)$  dependences for the  $\text{Pd}_{90}\text{Cu}_{10}\text{-H}$   $\gamma$ -samples as well as for the  $\text{Pd}_{80}\text{Cu}_{20}\text{-H}$  and  $\text{Pd}_{75}\text{Cu}_{25}\text{-H}$   $\gamma$ - and  $\gamma'$ -samples are close to the  $T_K(n)$  dependence for the Pd-H solutions [15].

Thus, one can ascertain that the replacement of palladium for copper as well as for other noble metals, silver [5] and gold [4], results in no essential changes in the  $T_K(n)$  dependence of the Pd-H  $\gamma$ -solutions in the case of sample hydrogenation under conditions close to thermodynamical equilibrium ones. What is more, within the limits of experimental error this  $T_K(n)$  dependence remains the same even for the ordered Pd-Cu-H  $\gamma'$ -solutions.

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