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Distortions of the F.C.C. Crystal Lattice of Pd₆₀Cu₄₀ Alloy Hydrogenated under High Pressure

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An irreversible phase transition accompanied by a tetragonal distortion of the metal sublattice is shown to occur at $5 \leq P_H \leq 20$ kbar and $T > 220$ °C in the Pd₆₀Cu₄₀-H system. The results of X-ray investigation enable one to assume the observed distortion of the metal sublattice to be associated with its partial atomic ordering.

Показано, что при $5 \leq P_H \leq 20$ кбар и $T > 220$ °C в системе Pd₆₀Cu₄₀-H происходит необратимое фазовое превращение, сопровождающееся тетрагональным искажением подрешетки металла. Результаты рентгенографического исследования позволяют предположить, что наблюдаемое искажение металлической подрешетки связано с ее частичным атомным упорядочением.

1. Introduction

The discovery of superconductivity in the Pd-H system at the atomic hydrogen-to-metal ratio $n \gtrsim 0.8$ [1] has aroused a considerable interest and caused an intensive investigation of the properties of hydrogen solid solutions on the base of palladium and its alloys (see, for example, the review [2]). Some of the most interesting results were obtained by Stritzker when implanting hydrogen into the disordered f.c.c. alloys of palladium with noble metals — copper, silver, and gold [3, 4]. Both with palladium and these alloys, the forming thin (≈ 1500 Å) hydrogenated layer of the metal became superconducting at a certain radiation dose, then the superconducting critical temperature T_k increased, reached the maximum value T_k^m , and began decreasing. The dependences of T_k^m upon the content of an alloying element in palladium for each of the Pd-Cu, Pd-Ag, and Pd-Au alloy systems were in turn curves with a maximum, the maximum values T_k^{mm} being equal to ≈ 16.6 , 15.6, and 13.6 K, respectively, that significantly exceeded $T_k^m \approx 8.8$ K for palladium.

Further reasearch on these systems has shown that if in the case of the Pd-H solutions the T_k^m — value for the samples obtained by implantation agrees well with the maximum values of T_k (at $n \rightarrow 1$) for the bulk homogeneous samples studied in a series of works (see [2]), no such an agreement is observed for the Pd-noble metal-H solutions. An investigation of the Pd-Ag alloy with 20 at% Ag and the Pd-Cu alloy with 40 at% Cu (these compositions are close to the optimum ones for obtaining highest T_k — values according to [3, 4]) hydrogenated at $P_H \leq 70$ kbar has revealed [5] that, in contrast to [3, 4], the dependence $T_k(n)$ for the Pd₈₀Ag₂₀-H solid solutions is close to that for the Pd-H solutions, and in the Pd₆₀Cu₄₀-H system at $n \gtrsim 0.6$ and $T \gtrsim 2$ K superconductivity is absent.

Thus, the results of [5] allow to assume the anomalously high T_k — values obtained when implanting hydrogen into the palladium-noble metal alloys to be due to peculiarities of metastable states occurring in the process of implantation. This assumption

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is consistent with the results of some theoretical works (see [3, 6] for references) as well as with those of an experimental study on low-temperature heat capacity of the $\text{Pd}_{80}\text{Ag}_{20}$ -H non-superconducting solid solutions [6], according to which the alloying of palladium with noble metals can cause no increase in T_k in the case of formation of hydrogen solid solutions with f.c.c. metal sublattice. The fact that the instability of the crystal lattice might play a significant role (due to softening some phonon modes and, accordingly, to increasing electron-phonon interaction) when obtaining high T_k — values at hydrogen implantation into palladium alloys with Cu, Ag, and Au, has been noted by Stritzker [2 to 4] who observed an interesting peculiarity of the dependence of T_k upon the dose Ψ of implanted hydrogen. In the Pd-Cu and Pd-Ag alloys with compositions close to the optimum one ($T_k^m > 15$ K) the monotonous growth of T_k with increasing Ψ was sometimes interrupted by its sudden drop and disappearance of superconductivity at $T > 1$ K, the residual resistance R_r decreasing by 10 to 20% in a jump-like manner. Further increase in Ψ caused a monotonous decrease in R_r , but no superconductivity has been observed above 1 K. Stritzker has explained this by the formation of a new non-superconducting phase having a lower value of R_r .

Thereby, the causes for the appearance of superconductivity with extremely high values of T_k when implanting hydrogen into the palladium-noble metal alloys proved to be closely connected with the structural peculiarities of these systems. It should be mentioned here that all the hydrogen solid solutions on the base of transition metals of VI-VIII groups investigated by now had either f.c.c. or h.c.p. metal sublattices (these are hydrides of iron [7], technetium [8], rhodium [9], chromium, manganese, cobalt, nickel, molybdenum, palladium, and of a series of their alloys, see reviews [10 to 12]). Since the palladium-noble metal alloys in question themselves possess f.c.c. structure, the structure of a hypothetical new phase forming at hydrogen implantation should differ principally from those observed earlier, that gives an additional urgency to its research.

So, we decided to test whether hydrogenation of massive Pd-Ag and Pd-Cu samples by means of a direct contact of the metal with molecular hydrogen (i.e. under conditions close to thermodynamic equilibrium) would also result in the formation of new phases. As in [5], the $\text{Pd}_{80}\text{Ag}_{20}$ and $\text{Pd}_{60}\text{Cu}_{40}$ alloys, having nearly optimum compositions according to [3, 4], had been chosen for the investigation.

2. Experimental

The samples in the form of discs with ≈ 5 mm diameter were cut from the same 0.2 mm thick foil which had been earlier used for sample preparation in [5]. This foil was prepared as follows. The ingots were melted in an induction furnace in vacuum from electrolytical Pd, Ag, and Cu. After a 6 h homogenization at 930 °C and water-quenching, these ingots were rolled at room temperature to the required thickness, then subjected to stress-relief annealing in vacuum at 930 °C for 5 min and again quenched in water. According to [13], the $\text{Pd}_{80}\text{Ag}_{20}$ and $\text{Pd}_{60}\text{Cu}_{40}$ alloys prepared in this way should have a disordered f.c.c. structure.

Hydrogenation of the samples was conducted by several hours exposure to high hydrogen pressure. In the case of the $\text{Pd}_{60}\text{Cu}_{40}$ alloy pressure up to 20 kbar were used. After complete hydrogenation, the high pressure chamber was cooled down to ≈ -25 °C, the pressure lowered to atmospheric, the sample were removed from the chamber and later on were kept in liquid nitrogen. Manipulations with the hydrogenated samples at $T \approx -25$ °C and atmospheric pressure were continued for not longer than 3 min. An examination showed that during 20 min any noticeable losses of hydrogen from the specimens were absent under these conditions. At liquid nitrogen

temperature no losses of hydrogen from the specimens occurred for two years at least. To obtain contents $n \approx 1$, hydrogenation of the Pd₈₀Ag₂₀ alloy was carried out at $P_{\text{H}_2} \leq 70$ kbar and $250 \leq T \leq 350$ °C during 8 h with subsequent quenching to ≈ -90 °C. At $P = 1$ bar a pronounced release of hydrogen from the Pd₈₀Ag₂₀-H specimens began at $T \approx -50$ °C.

The entire hydrogen content in the samples was defined in two stages. Firstly, they were placed in a sealed glass vessel pre-filled with silicon, having room temperature. Hydrogen was liberated partially from the specimens expelling silicon from the vessel. The pronounced release of hydrogen stopped after some hours. The quantity of hydrogen was measured with an accuracy $\delta n \approx 0.02$ by controlling its volume. Then the samples were placed in a pre-evacuated vessel with known volume and heated to a higher temperature. Annealing for 1 h at 300 °C proved to be sufficient for a complete hydrogen liberation from the specimens. In this case the hydrogen pressure in the vessel did not exceed 5 Torr, and its content in the metal was defined with an accuracy $\delta n \approx 0.04$. The fact that hydrogen had been completely liberated from the specimens (within $n \approx 0.01$) was checked up by placing a sample annealed at 300 °C again into the evacuated vessel and heating it to 500 °C. The analysis of hydrogen content was also conducted by another method: by the difference in the sample weights before and after annealing for 20 min at 450 °C in a vacuum of $\approx 10^{-5}$ Torr. The results obtained by these two methods were in good agreement. Thus, the total composition of the samples was determined with an accuracy $\delta n \approx 0.05$.

An X-ray study was carried out by a phototechnique using a DRON-1 diffractometer with filtered CuK α radiation. The diameter of the cylindrical film holder was 229.2 mm. The X-ray reflections were recorded at two fixed temperatures, -190 and $+20$ °C. In the case of recording at $T = -190$ °C, the hydrogenated samples which had been kept before in liquid nitrogen, were placed in a pre-cooled cryostat for X-ray measurements with no intermediate warming.

For the Pd₈₀Cu₄₀ alloy, the electroresistance behaviour at high hydrogen pressure had also been studied. The measurements were conducted by a conventional four-probe technique, the sample dimensions being $5 \times 1 \times 0.2$ mm³. The pressure was measured by a manganin wire gauge, the temperature by a chromel-alumel thermocouple with an accuracy of ± 0.5 kbar and ± 5 °C, respectively. During the process of measuring the temperature was kept constant to an accuracy ± 0.2 °C. The thermocouple and the manganin gauge were insulated against exposure to hydrogen.

3. Results and Discussion

Hydrogen forms with palladium wide ranges of interstitial solid solutions on the base of an f.c.c. metal sublattice. In the T - c diagram of the Pd-H system there is a cupola of separation into two isomorphous phases, γ_1 and γ_2 , the parameters of the critical point being $T_{\text{cr}} = (292 \pm 2)$ °C, $(P_{\text{H}_2})_{\text{cr}} = (19.7 \pm 0.2)$ bar, $n_{\text{cr}} = 0.250 \pm 0.005$ [14]. At room temperature the boundary of the two-phase region $n_{\gamma_2}^{\text{min}} \approx 0.6$. Alloying palladium with silver and copper lowers T_{cr} . At room temperature $n_{\gamma_2}^{\text{min}}$ decreases to ≈ 0.3 in the Pd₈₀Ag₂₀-H system [14]. In the Pd₅₀Cu₄₀-H system $T_{\text{cr}} \approx 20$ °C, and, hence, at $T > 20$ °C the solubility of hydrogen in the f.c.c. Pd₈₀Cu₄₀ alloy should be a continuous function of pressure [15].

An X-ray examination of the Pd₈₀Ag₂₀-H samples with $n \approx 1$ has shown them to have an f.c.c. metal sublattice with the lattice constant monotonously increasing with n . The values ΔV_0 of the jump in the unit-cell volume of the Pd₈₀Ag₂₀ alloy at hydrogenation agree satisfactorily with the dependence $\Delta V_0(n)$ for the f.c.c. palladium-based alloys presented in [12]. For example, the Pd₈₀Ag₂₀-H solution with $n =$

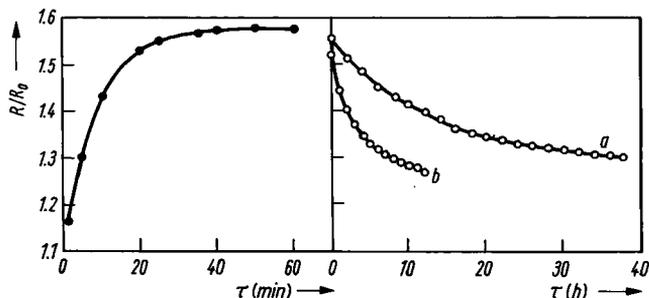


Fig. 1. Time dependences $R(\tau)$ of electroresistance of the $\text{Pd}_{60}\text{Cu}_{40}$ alloy in the course of exposures at $P_{\text{H}_2} = 10$ kbar and fixed values of temperature (see Section 3.1). $T = 200^\circ\text{C}$ (\bullet), 235°C (a), and 250°C (b). R_0 is the resistance of the sample at room temperature and atmospheric pressure

$= 0.97 \pm 0.05$ ($T_k = 6.08$ K that agrees well with the data of [5]) at $T = -190^\circ\text{C}$ had a lattice constant $a = (4.098 \pm 0.002)$ Å corresponding to $\Delta V_0 = (8.45 \pm 0.2)$ Å³. It should be noted that the absence of any new structural peculiarities in the $\text{Pd}_{80}\text{Ag}_{20}\text{-H}$ solid solutions was not surprising, for at a sufficiently high hydrogen content these solutions become superconducting, the dependence $T_k(n)$ being close to that for the Pd-H solutions [5], while the new phases in the Pd-Ag-H system obtained in [3] are not superconducting at $T > 1$ K.

With the $\text{Pd}_{60}\text{Cu}_{40}\text{-H}$ system, the surprises have begun already at studying the behaviour of electroresistance.

3.1 Electroresistance of the $\text{Pd}_{60}\text{Cu}_{40}$ alloy under high hydrogen pressure

In an inert medium (silicon) the resistance of this alloy increases weakly and monotonously with temperature (triangles in Fig. 2). In hydrogen at fixed T and P_{H_2} in the temperature range up to $\approx 220^\circ\text{C}$ a time drift $R(\tau)$ towards increasing R is observed. A typical dependence $R(\tau)$ at $T = 200^\circ\text{C}$ and $P_{\text{H}_2} = 10$ kbar is exhibited in Fig. 1 (close circles). It is seen from Fig. 1 that the resistance increases monotonously, reaches some limit value in ≈ 50 min, and further on is almost constant. An increase in electroresistance is typical for the formation of primary solutions, and the time drift is caused by the diffusion nature of this process in the case of the Me-H systems (similar dependences $R(\tau)$ were, for instance, observed at the formation of γ_1 -solutions Pd-H [16], Ni-H , and Ni-Me-H , where $\text{Me} = \text{Mn, Fe, Co, and Cu}$ [10, 11]).

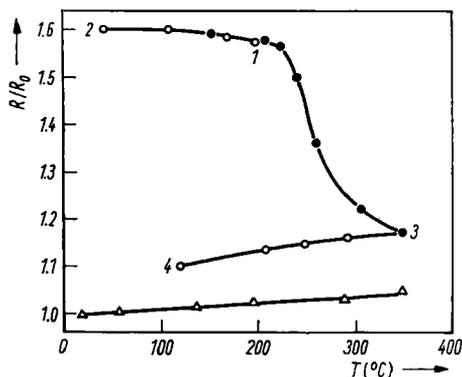


Fig. 2. Temperature dependences $R(T)$ of electroresistance of the $\text{Pd}_{60}\text{Cu}_{40}$ alloy at pressure 10 kbar. Δ in an inert medium (silicon); \bullet , \circ in hydrogen, at increasing and decreasing temperature, respectively. The $R(T)$ dependence in hydrogen atmosphere is taken in the sequence 1 \rightarrow 2 \rightarrow 3 \rightarrow 4 at a stepwise temperature increase and decrease with exposure at every fixed point during 2 h

In the case of sample hydrogenation at $T > 220$ °C, the view of the curve $R(\tau)$ changes. A rather fast increase in resistance at the initial part is followed by its slow decrease. The kinetics of the last process is illustrated by curves a and b in Fig. 1 obtained as follows. The sample was kept at 200 °C till the end of the resistance drift (≈ 1 h), then the temperature was sharply raised (a — to 235 °C, b — to 250 °C) and further on kept constant. The kinetics is seen to be accelerated with temperature, but even an exposure for tens of hours proves to be insufficient for the termination of the resistance drift. A similar picture is observed at higher temperatures (up to 350 °C), too.

Fig. 2 represents an isobar ($P_{H_2} = 10$ kbar) of the Pd₆₀Cu₄₀ alloy electroresistance in hydrogen atmosphere taken in the process of a step-wise increase and decrease in temperature with an exposure for 2 h at every fixed T -value (the final values of R are given in the figure). Firstly, the sample was hydrogenated at 200 °C, then cooled down to 44 °C (segment 1-2), heated to 350 °C (2-3), and cooled (3-4) again. One can see that the initial manipulations at $T \leq 200$ °C (cooling and heating) lead to no essential irreversible changes of R . At a further increase in temperature the resistance begins decreasing sufficiently, at $240 \leq T \leq 280$ °C it drops most sharply, and then the dependence $R(T)$ becomes smoother. A subsequent step-wise temperature decrease (segment 3-4) causes a further decrease in resistance, the time drift $R(\tau)$ in the process of exposures at fixed temperature values being nearly absent. An irreversible change in electroresistance shows that when heating higher than ≈ 200 °C there occurs an irreversible phase transformation in the samples under study.

The kinetics of this transformation is slow. Two peculiarities in the resistance behaviour at $T > 220$ °C must be noticed. (i) At heating an exposure of the sample to higher temperatures results in a lower final value of R (Fig. 1, curves a and b). (ii) While cooling after heating to the maximum temperature (Fig. 2, segment 3-4) there occurs almost no time drift $R(\tau)$. Such a behaviour of the resistance is likely to be due to the fact that owing to kinetical reasons the degree of the observed phase transformation increases with temperature in the case of exposures during reasonable periods of time. It should be noted that the temperature T^* at which the transformation starts (≈ 220 °C), seems also to be determined by kinetics and is independent of pressure at $5 \leq P_{H_2} \leq 20$ kbar within ± 20 °C (a similar scatter in the T^* -value is observed when repeating the measurements for one and the same magnitude of pressure).

3.2 X-ray data

The initial Pd₆₀Cu₄₀ alloy has an f.c.c. lattice with the lattice constant (see Table 1, line 1) coinciding well with that given in [17]. The X-ray study of the Pd₆₀Cu₄₀-H samples obtained by exposure to $5 \leq P_{H_2} \leq 20$ kbar and temperatures both higher and lower than T^* of the beginning of the phase transformation discovered when studying the electroresistance, was performed at $T = -190$ °C. The study has shown that the metal sublattice of the samples obtained by a 6 h exposure at $T = 200$ °C $< T^*$ with compositions $n \leq 0.47$, maintains f.c.c. symmetry (a γ -solution forms), the ΔV_0 -values of the jump in the unit-cell volume of the Pd₆₀Cu₄₀ alloy at hydrogenation being in satisfactory agreement with the dependence $\Delta V_0(n)$ for γ -solutions of hydrogen in palladium and its alloys presented in [12]. The data for the sample with the maximum hydrogen content are given in Table 1, line 2. A diffraction pattern for the samples hydrogenated at $T = 200$ °C exhibits, however, some peculiarities: the lines of $\{111\}$ type are sharp, whereas the others are significantly broadened, which can be interpreted as a result of small tetragonal or orthorhombic distortions, or merely of the appearance of packing defects in close-packed planes [18].

Table 1

sample number	treatment conditions	n	X-ray study temperature (°C)	crystal structure	a (Å)	c (Å)	c/a	V_a (Å ³)*
1	initial sample	0	20	γ	2.793 ± 0.002	—	—	13.64 ± 0.02
2	exposure for 6 h at 200 °C and $P_{H_2} = 20$ kbar	0.47	-190	γ	3.897 ± 0.005	—	—	14.80 ± 0.05
3	exposure for 10 h at 300 °C then for 6 h at 200 °C ($P_{H_2} = 20$ kbar)	0.57	-190	γ'	3.958 ± 0.008	3.828 ± 0.012	0.967 ± 0.004	14.99 ± 0.07
4	annealing of the sample No. 3 for 48 h at 20 °C and $P = 1$ bar	0.34	20	γ'	3.954 ± 0.005	3.733 ± 0.008	0.944 ± 0.002	14.59 ± 0.05
5	annealing of the sample No. 4 for 6 h at 300 °C in vacuum	0	20	γ'	3.855 ± 0.005	3.660 ± 0.008	0.949 ± 0.002	13.60 ± 0.05

*) $V_a = a^3/4$ and $a^2c/4$ for γ and γ' structures, respectively.

The Pd₆₀Cu₄₀-H samples obtained by a 10 h exposure at $250 \leq T \leq 350$ °C (i.e. at $T > T^*$) and $P_{H_2} \leq 20$ kbar, had the metal sublattice which may be described on the base of a face-centred tetragonal pseudo-cell (further on a γ' -solution). The hydrogen content in these samples was in the range $0.3 \lesssim n \lesssim 0.5$, the volume V_a per metal atom had approximately the same value as that for the Pd₆₀Cu₄₀-H γ -solutions with near n -values. However, it should be mentioned here that the diffraction lines of the γ' -phase were broadened; V_a and c/a magnitudes varied significantly from sample to sample depending upon treatment conditions under high hydrogen pressure as well as for different samples obtained in the same conditions in successive series of experiments, and were within the limits $14.6 \lesssim V_a \lesssim 15.3$ Å³, $0.94 \lesssim c/a \lesssim 0.97$. These phenomena seemed to be associated with the differences in the degree of completeness of the $\gamma \rightarrow \gamma'$ transformation and, thus, to be due to kinetical reasons (see the previous section). Note, besides, that the exposure at lower temperature (down to 235 °C $> T^*$) but during longer periods of time (≈ 30 h) also resulted in the formation of the γ' -phase.

The $\gamma \rightarrow \gamma'$ transformation, as was shown at studying the electroresistance behaviour (Section 3.1), is irreversible in character. This gives an opportunity to compare hydrogen solubilities in the γ and γ' phases under the same conditions. With this aim in mind, at $P_{H_2} = 20$ kbar the sample was at first transformed into the γ' -state at $T = 300$ °C $> T^*$ and then kept for 6 h at $T = 200$ °C. The X-ray data for the sample obtained in this way are listed in Table 1, line 3. As one can see from the comparison with the data for the γ -sample (cited in the same table, line 2), the solubility of hydrogen at $P_{H_2} = 20$ kbar and $T = 200$ °C is somewhat higher in the γ' -phase of the Pd₆₀Cu₄₀-H solid solution than in the γ -phase.

Interesting results were obtained from the research on quenched γ' -samples in the process of their annealing leading to the liberation of hydrogen. At a partial hydrogen release from the samples after annealing at room temperature and atmospheric pressure, their metal sublattice retained its tetragonal symmetry, the c/a values generally decreasing (a typical example is given in Table 1, line 4). The alloy maintained the tetragonal structure after the 6 h annealing in vacuum at 300 °C, too, that involved a *complete* release of hydrogen (see Section 2), while the V_a magnitude decreased to a value close to that for the initial Pd₆₀Cu₄₀ f.c.c. alloy (Table 1, line 5). Further annealing for some hours at $T \geq 350$ °C brought the alloy structure back to the initial cubic one. The recovery of the f.c.c. structure occurred also after plastic deformation of the Pd₆₀Cu₄₀ γ' -sample at room temperature. These results demonstrate the fact that at atmospheric pressure and $T \gtrsim 20$ °C the γ' -structure of the Pd₆₀Cu₄₀ alloy is not a thermodynamically equilibrium one. At the same time, metastability of this structure after a full release of hydrogen and even some increase in the degree of its tetragonality seem to be favourable for the assumption that the observed tetragonal distortions are mainly connected to the rebuilding of the metal sublattice itself occurring in the Pd₆₀Cu₄₀-H solution rather than to a possible phase transformation in the hydrogen sublattice (e.g. its ordering).

One of the possibilities for such a rebuilding is an atomic ordering. The presence of wide regions of substitutional solid solutions with ordered atom distributions is characteristic of the T - c diagram for the Cu-Pd system [17] as well as for a series of related systems (e.g. Cu-Au and Cu-Pt [19]), and there are generally some regions of ordering conforming to the A₃B, AB, and AB₃ stoichiometry. In particular, it is precisely the tetragonal distortion of the f.c.c. lattice of Cu-Pd alloys which the ordering in the range of compositions close to Cu₃Pd gives rise to [17, 20, 21] (it is worth pointing out that as in our case, the degree of tetragonality depended greatly on a kinetical factor at a partial ordering of the Cu₃Pd alloy [21]). If ordering of this type takes

place, there appear superstructural diffraction lines in addition to the basis (structural) ones, the position of the former being near to that for reflections from the planes with mixed indices. For the Pd-Cu alloys, the ratio between the structural factors for the superstructural and basic reflections is $\approx 1:100$ [20], which complicates a rigorous demonstration of the existence of ordering using X-ray data for polycrystalline samples. Nevertheless, for the γ' -samples in addition to the basic lines for the f.c.t. quasicell there were observed some very weak and very broad lines to which the mixed indices may be attributed. The (110) line was the brightest one among them in agreement with the data of [20]. The results of the most successful study for the Pd₆₀Cu₄₀ γ' -alloy (with no hydrogen) are represented in Table 2.

Thus, it is rather safe to state on the basis of X-ray data that the formation of the γ' -phase in the Pd₆₀Cu₄₀-H system is accompanied by an ordering of the metal sublattice, though not complete as is revealed by the large width of superstructural lines compared to that of the basic ones. The appearance of packing defects in close-packed planes of the metal sublattice of the γ -phase forming at lower temperatures (which manifests itself in the broadening of all the diffraction lines except for {111}) is likely to be an intermediate stage of this process. The question about ordering needs, however, an additional investigation, and work in this field is in progress.

Table 2

X-ray data for the sample No. 5 (see Table 1).*) $T = 20^\circ\text{C}$, CuK $_{\alpha}$ radiation

No.	d_{exp} (Å)	I_{exp}	Q_{exp} (Å ⁻²)	hkl	Q_{cal} (Å ⁻²)
1	3.986	t	629	100	673
2	3.604	t	770	001	747
3	2.722	vw	1350	110	1346
4	2.196	vs	2074	<u>111</u>	2092
5	1.933	vs	2676	<u>200</u>	2692
6	1.859	m	2894	<u>002</u>	2986
7	1.698	t	3468	201	3438
8	1.542	t	4206	121	4111
9	1.492	t	4492	112	4332
10	{1.347	vs	5511	<u>220</u>	5383
11	{1.328	vs	5670	<u>202</u>	5678
12	1.272	t	6181	221	6130
13	1.206	t	6876	130	6729
14	1.1566	s	7475	<u>131</u>	7476
15	1.1240	vw	7915	<u>113</u>	8064
16	1.0921	w	8384	<u>222</u>	8369
17	1.0293	t	9439	023	9410
18	1.0071	t	9859	312	9715
19	0.9627	vw	10790	<u>400</u>	10766
20	0.8801	w	12910	<u>331</u>	12859
21	0.8671	m	13300	{ <u>133</u>	13448
				{ <u>420</u>	13458
22	0.8555	m	13663	<u>402</u>	13752
23	0.8314	t	14467	412	14425
24	0.7803	w	16424	<u>422</u>	16444

*) Calculation is conducted for the tetragonal cell with $a = 3.855 \text{ \AA}$, $c = 3.660 \text{ \AA}$. The indices of the f.c.t. pseudo-cell are underlined $Q = (1/d^2) \times 10^4$, exp = experimental, cal = calculated, vs = very strong, s = strong, m = medium, w = weak, vw = very weak, t = trace.

Going back to Section 1, it can be stated that the study of the Pd₆₀Cu₄₀-H system has actually led to the discovery of a new phase transformation having no analogues in the metal-hydrogen systems investigated earlier. Now it is difficult to say definitely whether the γ' -phase occurring under high hydrogen pressure is the very non-superconducting phase which forms sometimes when implanting hydrogen and the existence of which may account for the anomalously high values of superconducting critical temperature T_k observed [4]. There are, nevertheless, some arguments for the possibility of an affirmative answer. The formation of the γ' -phase as well as that of the non-superconducting one at implantation is accompanied by a drop in electroresistance (see Fig. 2). Great local overheatings in the course of hydrogen implantation and a high concentration of defects in the obtained hydrogenated layer produce favourable conditions for diffusional processes to occur. As for the Pd-Ag-H system where the same phenomena as in the Pd-Cu-H system should take place according to [3, 4], the absence of tetragonal distortions in the Pd₈₀Ag₂₀-H samples obtained in the present work may be, for instance, due to just kinetical reasons, if the temperature of the $\gamma' \rightarrow \gamma$ transformation is considerably lower than 250 °C at which hydrogenation of the samples was conducted (see Section 2). Paper [22] should also be mentioned here where attention is drawn to a possible connection between the values of the optimum Pd-Cu, Pd-Ag, and Pd-Au alloy concentrations for obtaining highest T_k at hydrogen implantation and those being most favourable for an ordering to occur in the alloys with no hydrogen.

4. Conclusions

Under high hydrogen pressure an irreversible phase transformation takes place in the Pd₆₀Cu₄₀-H solid solution. This transformation is accompanied by a tetragonal distortion of the f.c.c. metal sublattice which is likely to be due to its ordering. The available data allow one to conclude that the lattice instability with respect to the transition into just this phase may be responsible for the anomalous behaviour of superconducting properties when implanting hydrogen into the Pd-Cu alloys. The study has also revealed just one more fact associated with the uniqueness of hydrogen as a component of a metallic system. Due to the high diffusional mobility of hydrogen in metal it proved possible to obtain at normal conditions metastable Pd₆₀Cu₄₀ specimens with tetragonal structure, removing hydrogen from the Pd₆₀Cu₄₀-H solution by annealing in vacuum at temperatures where no transition of the metal lattice to the equilibrium f.c.c. structure occurs by kinetical reasons.

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