
**METALS
AND SUPERCONDUCTORS**

Superconductivity in the Zr–D System under Pressure

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Abstract—The superconducting transition temperature T_c of the $ZrD_{0.48}$ alloy is measured in the pressure range up to 41.5 GPa. The measurements are carried out in a high-pressure chamber with diamond anvils by the inductometric method. It is found that $T_c(P)$ increases to 3.1 K at a pressure below 30 GPa, exhibits a sharp increase up to 8 K near 30 GPa, and then smoothly decreases to ~6.5 K at 41.5 GPa. A similar dependence $T_c(P)$ is obtained for pure Zr. The similarity of the $T_c(P)$ curves suggests that the dependence $T_c(P)$ observed for $ZrD_{0.48}$ is due to the presence of ω -phase in this alloy at pressures $P < 30$ GPa and the ω – β transition at $P \approx 30$ GPa, which leads to the establishment of new ratios between the phases in the Zr–D system. In the pressure range studied, no indications are observed for new superconducting phases similar to the phases of intermediate composition in the Ti–H(D) system, which are formed by the hydrogen transfer from tetrahedral to octahedral interstitials. © 2000 MAIK “Nauka/Interperiodica”.

In the phase T – c diagram of the Zr–H system at atmospheric pressure, four phases are believed to be in equilibrium [1]: the solid solution of hydrogen in hexagonal close-packed (hcp) α -Zr, the hydrogen solid solution based on the body-centered cubic (bcc) high-temperature phase β -Zr, the nonstoichiometric dihydride δ -ZrH_{2–y} with the face-centered cubic (fcc) sublattice of Zr, and the ϵ -ZrH_{2–y} dihydride with the homogeneity region extending up to the stoichiometric composition $x = H/Zr = 2$. The ϵ -phase is formed from the δ -phase due to its tetragonal distortion accompanied by an increase in the hydrogen content. The high-temperature phase β -ZrH_x is in an eutectoid equilibrium with α -Zr(H) and δ -ZrH_{2–y} at a point with the coordinates $T = 550^\circ\text{C}$ and $x = 0.5$. Recent studies [2–5] indicate that one more phase, namely, γ -ZrH with the face-centered orthorhombic sublattice of Zr, also has the stability region at temperatures below $\sim 235^\circ\text{C}$ and slowly arises in the two-phase alloys ($\alpha + \delta$)-ZrH_x even at room temperature.

In all these phases, the hydrogen atoms occupy the tetrahedral interstitials (tetrapores) of the Zr sublattice. The problem of hydrogen transfer from tetrapores to octapores in Zr hydrides under pressure has already been discussed in the literature [5, 6]. In the Ti–H system, which is an analog of the Zr–H system at atmospheric pressure [7–10], such a transfer occurs under a pressure of 2.05 GPa [11, 12]. In the composition range close to the eutectoid composition ($x = 0.7$ – 0.9), the hydrogen transfer gives rise to a new phase, which, after the quenching under pressure in liquid nitrogen, remains metastable up to atmospheric pressure. In the metastable state, the new phase is characterized by the superconducting transition temperature $T_c = 4.3$ K and also by the reverse isotropic effect ($T_c = 5.0$ K in the

Ti–D system) [13, 14]. Empirical estimates of the pressure of the tetra–octa transition for hydrogen in the Zr–H system gave values from 45 [6] to 58 GPa [5]. However, these estimates disregarded the electronic transition in pure Zr under a pressure of 30 GPa [15–18], which is attended by an increase in the metallic radius. The existence of electronic transition in pure Zr decreases the reliability of the estimates obtained in [5, 6] and stimulates interest in the direct experimental measurements. The structural measurements were performed with zirconium dihydride under pressures up to 18 GPa [6, 19], which showed the absence of phase transformations.

The aim of the present work was to carry out the measurements of the superconducting properties of alloys in the zirconium–hydrogen system in the pressure range extended through the use of chambers with diamond anvils and also to verify experimentally whether the new phases, whose existence can be connected with the tetra–octa transfer of hydrogen, are formed in this system under pressures up to ~ 40 GPa. As the temperature T_c in the Ti–H(Ti–D) system exhibits a reverse isotope effect, we studied the deuteride alloy $ZrD_{0.48}$, which is close in composition to the eutectoid alloy in the Zr–H(D) system ($x = 0.5$ [1]).

1. EXPERIMENTAL TECHNIQUE

The initial alloy of chemical composition D/Zr = 0.48 ± 0.01 was prepared by the saturation of high-purity (~ 99.96 at. %) zirconium with a gaseous deuterium obtained by heating of a TiD₂ sample (for more detail, see [5]). The deuterium content was determined by the weighing method.

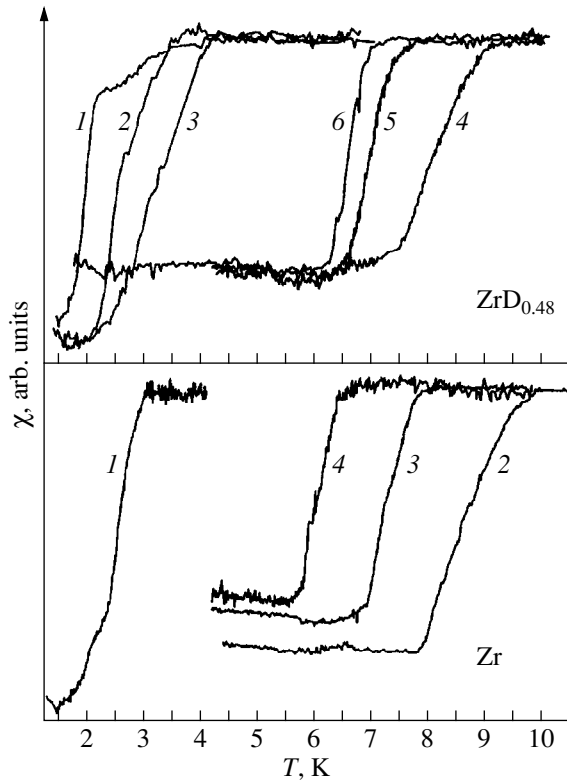


Fig. 1. Experimental temperature dependences of the magnetic susceptibility upon heating of the $\text{ZrD}_{0.48}$ sample at pressures of (1) 17.9, (2) 23.5, (3) 28.9, (4) 30.1, (5) 36.5, and (6) 41.5 GPa and the pure Zr sample at pressures of (1) 21.7, (2) 29.7, (3) 36.7, and (4) 43 GPa.

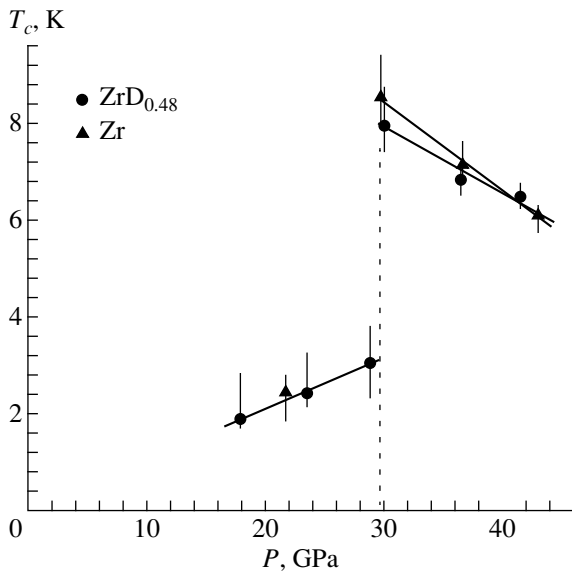


Fig. 2. Pressure dependence of the superconducting transition temperature for $\text{ZrD}_{0.48}$ and pure Zr. Short lines indicate the transition temperature ranges. The dotted line corresponds to the ω - β transition in Zr.

High pressures were produced using an apparatus with diamond anvils, which was fabricated from the non-magnetic materials [20]. A sample and crystals of ruby reference specimen were mounted in the orifice of a metallic gasket with diameter of 0.15 mm. The methanol-ethanol mixture in the ratio 4 : 1 serves as a medium transferring the pressure. The change in pressure and its measurement were performed at room temperature. The pressure was determined from the shift of the ruby R -line with an accuracy of ± 0.05 GPa. The superconducting transition was determined from the ac measurements of the magnetic susceptibility $\chi(T)$ [21]. The amplitude of the alternating magnetic field with a frequency of 5.2 kHz was equal to 0.3 Oe. The high-pressure apparatus was entirely cooled in a cryostat down to 1.5 K, and the recording of the $\chi(T)$ curve was performed upon heating. The (Cu-Fe)-Cu thermocouple was used to measure the temperature with an accuracy of ± 0.2 K. Since the apparatus required the preliminary warming-up for a pressure change and its determination, the measuring cycle for each pressure took a day.

2. RESULTS

The temperature dependences of the magnetic susceptibility $\chi(T)$ for the $\text{ZrD}_{0.48}$ alloy in the range $17.9 \leq P \leq 41.5$ GPa are shown in Fig. 1. Abrupt changes in $\chi(T)$ caused by the superconducting transitions in $\text{ZrD}_{0.48}$ are clearly seen in the curves. In the data processing, the superconducting transition point T_c was determined as a temperature at which the $\chi(T)$ jump reached its half-height. The temperatures between which the jump magnitude changed from 10 to 90% were taken as the temperature boundaries of the transition region. Thus determined temperatures and temperature ranges of the superconducting transitions as functions of pressure are given in Fig. 2. It is seen from the figure that T_c monotonically increases with pressure in the range up to ~ 29 GPa. A jumpwise increase in T_c by about 5 K is observed at a pressure of 30.1 GPa, and then the dependence $T_c(P)$ becomes a decreasing function.

A similar dependence $T_c(P)$ was obtained earlier for pure Zr with the help of electrical resistance measurements [18]. The resistivity data usually somewhat differ from the results obtained with the help of magnetic susceptibility measurements; hence, we repeated our measurements for the initial Zr material, from which the deuteride was prepared. The experimental curves $\chi(T)$ for pure Zr are given in the lower part of Fig. 1, and the results of the curves processing are presented in Fig. 2 together with the data for $\text{ZrD}_{0.48}$. It is seen from Fig. 2 that the $T_c(P)$ curves for pure Zr and $\text{ZrD}_{0.48}$ coincide to within the spread of experimental points. A certain correlation between our data and the results obtained in the earlier studies on the T - P diagram of the Zr-H(D) system under a pressure up to 7 GPa [5] and the phase transitions in pure Zr in the pressure range up to 70 GPa

[15–18, 22–24] allows us to make a number of suggestions about the phase transformations in the Zr–H(D) system in the pressure range $P \leq 41.5$ GPa.

3. DISCUSSION

Under pressure, pure zirconium undergoes a number of phase transitions [22]. In the T – P phase diagram of Zr in the ranges $P \leq 6.5$ GPa and $T \leq 900^\circ\text{C}$, the α – β phase boundary has a negative slope up to the triple point with the coordinates $P = 5.5$ GPa and $T = 700^\circ\text{C}$, at which α -Zr, β -Zr, and the high-pressure hexagonal phase ω -Zr are in an equilibrium [23]. In the compression experiments with shear [24], the equilibrium pressure of the α – ω transition at room temperature was determined as $P = 2.2$ GPa. However, under quasi-hydrostatic pressure, the $\alpha \rightarrow \omega$ transition occurs at 4–7 GPa owing to the hysteresis [18, 23]. Near $P = 30$ GPa, ω -Zr at room temperature transforms into the bcc phase [15–17], and then experiences an isomorphic transition near 56 GPa [17]. The ω – β transition at $P = 30$ GPa is followed by the jumpwise increase in T_c [18]. According to [15–18], the structural transformations and the T_c jump under ultrahigh pressure are due to the s – d electronic transition, as a result of which the electronic configuration of Zr becomes similar to the configurations of the bcc Group V metals.

In the T – P phase diagram of the Zr–H (Zr–D) system studied in the ranges $P \leq 7$ GPa and $T \leq 700^\circ\text{C}$, a curve of the phase equilibrium new for this system, the temperature of which increases with pressure, has been found at pressures above 4 GPa [5]. The X-ray powder diffraction analysis of the samples quenched up to 80 K under a pressure of 5–6 GPa showed that this curve is the boundary for the new (second) eutectoid equilibrium involving the ω -, δ -, and ε -phases. Its appearance is explained by the fact that, under pressure, the region of existence of the fcc δ -ZrH(D) $_{2-y}$ dihydride narrows to zero, and the temperature of intersection of the δ -phase homogeneity boundaries at the second eutectoid point increases with pressure [5].

Therefore, in the ZrD $_{0.48}$ alloy close in composition to the eutectoid, the ω -phase with a low hydrogen content and the ε -ZrD $_{2-y}$ dihydride should coexist at pressures above 7 GPa and at room temperature. The close values of $T_c(P)$ for ZrD $_{0.48}$ and pure Zr (Fig. 2) suggest that, in the range up to 30 GPa, the superconductivity of ZrD $_{0.48}$ is due to the presence of the ω -phase, whereas the hydrogen-rich phase, most likely, the ε phase, remains nonsuperconducting. From this fact, it can be concluded with confidence that new superconducting phases, whose appearance can be related to the hydrogen transition from tetrapores into octapores, are not formed in the Zr–D system at pressures up to 30 GPa.

The superconducting transition temperature jump near 30 GPa in ZrD $_{0.48}$ is likely caused by the transformation of the ω -phase in the alloy into the bcc phase. Two most probable variants can be considered for the

distribution of hydrogen in the alloy above this transition. In the first case, the β -phase in the Zr–D system at low temperatures and pressures above 30 GPa is depleted in hydrogen and coexists with the nonsuperconducting hydride, ε -ZrD $_{y-2}$, in which virtually all hydrogen is concentrated. Such an impurity distribution explains in a simple way the similarity in the behavior of $T_c(P)$ for ZrD $_{0.48}$ and pure Zr. However, it seems rather strange, since hydrogen dissolves in both β -Zr and the bcc Group V metals over a wide range of concentrations. The numerous ordered phases are formed in solid solutions of hydrogen in the bcc Group V metals at low temperatures [25]. It can be assumed that, in the Zr–D system, a hydrogen solid solution based on the bcc β -Zr phase is formed above 30 GPa and undergoes ordering at low temperatures. In this case, the coincidence of superconducting transition temperatures in pure metal and its alloy with hydrogen seems to be unusual. In both cases, the superconducting properties of ZrD $_{0.48}$ above 30 GPa can be explained without invoking the tetra–octa transition of hydrogen. However, the question on the presence of this transition in the Zr–H(D) system can be solved unambiguously only with the help of compression structural studies.

Thus, it is shown that pressure dependences of superconducting transition temperatures in the alloy of eutectoid composition ZrD $_{0.48}$ and in pure Zr in the range up to 41.5 GPa virtually coincide. This evidences for the presence of the two-phase ω -Zr(D) + ε -Zr(D) ~ 2 state in ZrD $_{0.48}$ at $P < 30$ GPa. The jumpwise increase in T_c near $P = 30$ GPa is likely connected with the ω – β transition resulting in the appearance of new phase ratios in the Zr–D system. The experimental dependence $T_c(P)$ gives no evidence of the existence of hydrogen transfer from tetrapores to octapores in the Zr–D system under a pressure up to 41.5 GPa.

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