Superconductivity in the Ti–D system under pressure

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(Submitted April 7, 1998; resubmitted June 15, 1998)
Fiz. Tverd. Tela (St. Petersburg) **40**, 2153–2155 (December 1998)

The pressure dependence of the superconducting transition temperature in $TiD_{0.74}$ has been measured up to 30 GPa in a diamond high-pressure chamber. It is found that the deuteride $TiD_{0.74}$ becomes a superconductor at pressures corresponding to the transition to the high-pressure ζ phase, with a transition temperature that increases from 4.17 to 4.43 K in the interval $P=14$–30 GPa. The value extrapolated to atmospheric pressure $T_c(0)=4.0$ K is significantly lower than the superconducting transition temperature ($T_c=5.0$ K) measured earlier in the metastable state obtained by quenching $TiD_{0.74}$ under pressure. It is assumed that the significant difference of the extrapolated value from the superconducting transition temperature in the metastable state after quenching under pressure is caused by a phase transition on the path from the stability region of the ζ phase under pressure to the region of the metastable state at atmospheric pressure. [S1063-7834(98)00212-3]

The $T-c$ diagram of the Ti–H (Fig. 1) and Ti–D systems at atmospheric pressure includes the eutectoid equilibrium of the α, β, and δ phases, based on the hexagonal close-packed (hcp), body-centered cubic (bcc), and face-centered cubic (fcc) titanium sublattices, respectively.[1–3] A new phase, ζ,[2,3] appears at a pressure of 2.05 GPa (3.4 GPa in the deuterides) and a temperature of $\sim$560 K in the alloy of eutectoid composition ($x=$H(D)/Ti$\approx$0.74). The structure of the ζ phase directly under pressure has been determined only by an x-ray method: It was found that, at $P\approx 5$ GPa, in the temperature interval $T=520$–720 K, the metal atoms in the ζ phase are packed into a face-centered tetragonal (fct) sublattice with a parameter ratio of $c/a=0.89$.[2] In order to study the properties of the new phase in more detail, it was quenched to 80 K after heat treating the samples at $T\geqslant 560$ K under a pressure above 5 GPa. After quenching under pressure, the single-phase state remained metastable at temperatures below 95 (100) K all the way to atmospheric pressure.[4] The structural characteristics of the metastable quenched state have been studied in detail at $T\leqslant 90$ K by inelastic neutron scattering and diffraction.[3,5–7] In this state, the hydrogen statistically occupies octahedral interstitial sites of the fct titanium sublattice,[7] unlike phases that are stable at $P=1$ atm, where the hydrogen is always located at tetrapores.[1,6] Since the specific volumes of the ζ phase and the metastable quenched state were extremely close to each other and much less ($\sim$10%) than in the other hydride phases of this system, it was assumed that, in the ζ phase, the hydrogen also was distributed over the octopores.[2,7] However, the ratio of the lattice parameters in the state after quenching was appreciably closer to unity than in the ζ phase, $c/a=0.95$.[7] It was therefore assumed[2,7] that the hydrogen distribution over the octopores can be different in the ζ phase than in the state after quenching, and the metastable quenched state was given an independent designation—the χ phase.

The difference in crystal structure must be reflected in the structure-sensitive physical properties. One of the clearest features of the χ phase is superconductivity with a transition temperature that is high for the Ti–H(D) system [$T_c=4.3\,(5.0)$ K],[8,9] which is a result of the transition of the hydrogen into the octopores. The superconductive properties of the χ phase have not previously been studied *in situ*. For this paper, we measured the pressure dependence of the superconducting transition temperature in ζ-$TiD_{0.74}$ up to 30 GPa and found that extrapolating the $T_c(P)$ dependence for the ζ phase to atmospheric pressure gives a value lower than was determined earlier for the χ phase. The measurements were made on the deuteride, since it has a higher superconducting transition temperature than does the hydride.

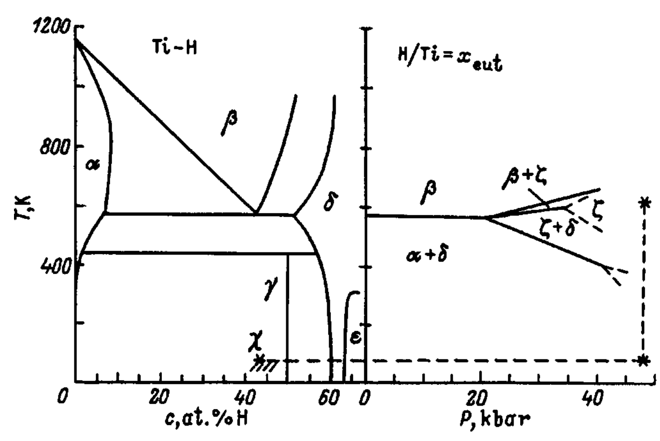

FIG. 1. Phase diagram of Ti–H. On the left is the $T-c$ projection for atmospheric pressure, and on the right is the $T-P$ projection for the hydrides of the near-eutectoid state.[3] The dashed lines denote the thermobaric treatment of the ζ phase and the unloading that results in the synthesis of the χ phase (its region of metastability at $P=1$ atm is hatched). On the $T-P$ projection, the low-temperature boundary of the region of the ζ phase ends with a dashed bifurcation, representing the region where the existence of a second high-pressure phase is probable.

1. TECHNIQUE

The initial two-phase deuteride of chemical composition $D/Ti = 0.74 \pm 0.01$ was synthesized by the reaction of high-purity (~ 99.98 at.%) titanium with deuterium gas, given off by heating TiD_2 (see Ref. 10, for example, for more details). The deuterium content was determined by weighing. In order for the small fabricated samples $\sim 0.1 \times 0.1 \times 0.03$ mm to maintain the average chemical composition, it was required that the microstructure of the two-phase deuteride be homogeneous and fine-grained. The limiting comminution of a crystalline grain (the characteristic size of the Ti precipitates in the matrix of the γ phase was[11] $\leqslant 100$ Å) was accomplished by heat-treating and quenching to 80 K a pellet of $TiD_{0.74}$ under a pressure of 6.5 GPa, followed by decay of the quenched χ phase when the sample was quickly returned to normal conditions.

An apparatus with diamond anvils fabricated from nonmagnetic materials was used to create high pressures.[12] The sample and crystals of a ruby standard were placed in the aperture of a metallic gasket 0.15 mm in diameter. A 4:1 methanol–ethanol mixture served as a pressure-transmission medium. The pressure was varied and measured at room temperature. The pressure was determined to within ± 0.05 GPa from the shift of the R line of ruby. The superconducting transition was determined from ac measurements of the magnetic susceptibility $\chi(T)$.[13] The amplitude of the variable 5.2-kHz magnetic field was 0.3 Oe. The high-pressure apparatus was cooled as a whole to 1.5 K in a cryostat, and the measurements of $\chi(T)$ were made while heating, using a (Cu–Fe)–Cu thermocouple to measure the temperature to within ± 0.2 K. Because of the necessity of repeatedly heating the apparatus to vary and determine the pressure, a measurement cycle at each pressure took days.

2. RESULTS AND DISCUSSION

In the range $P \leqslant 7$ GPa in which the $T-P$ diagram of the Ti–D system was studied earlier,[2] the line of the transformation into the ζ phase was located at temperatures above 450 K. Extrapolating this line makes it possible to estimate the transition pressure into the ζ phase when the sample is loaded at room temperature as approximately 10 GPa. The first measurement cycle of $\chi(T)$ was therefore carried out at a pressure of 9.5 GPa. No superconducting transition was observed in this cycle. In the next cycle, under a pressure of $P = 11.8$ GPa, an anomalous superconducting transition on the $\chi(T)$ isobar was clearly evident, although the jump is rather smeared out and has a low-temperature tail (Fig. 2). A further increase of the pressure to 30 GPa results in an increase of the superconducting transition temperature, while the jump becomes sharper and increases somewhat in magnitude. As the pressure is decreased, the superconducting transition becomes still more distinct than in the process of loading the chamber. However, after the pressure is reduced from 11.2 to 8.2 GPa, the superconductivity in the sample completely disappears, which is obviously associated with the decay of the ζ phase at room temperature to the low-pressure phase.

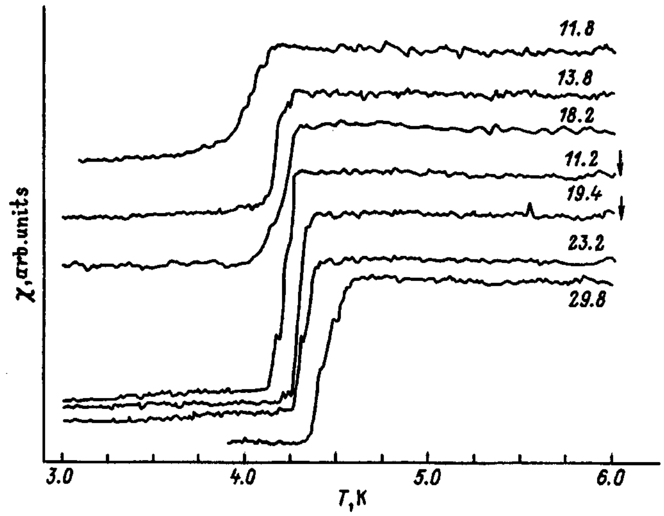

FIG. 2. Experimental curves of the temperature dependence of the magnetic susceptibility of $TiD_{0.74}$ under conditions of heating at fixed pressures (indicated in GPa near the curves). The arrows show curves recorded during unloading of the high-pressure chamber.

The temperature at which the jump in $\chi(T)$ reaches one half was taken as the superconducting transition point. The superconducting transition temperatures determined in this way are shown in Fig. 3 as a function of the pressure. It can be seen from this figure that the $T_c(P)$ dependence is close to linear in the region $P > 12$ GPa. On one hand, the deviation of the initial load point $P = 11.8$ GPa from a linear dependence, as well as the smearing of the jump of $\chi(T)$, can be regarded as evidence that the transition into a phase with superconducting properties was incomplete. On the other hand, when the $T-P$ diagram of the Ti–H system above 4 GPa was studied, bifurcation of the anomalies of the electrical resistance and the thermal effects of the transition into the ζ phase was observed, and, based on this, the possibility that a second high-pressure phase exists was indicated.[2] The

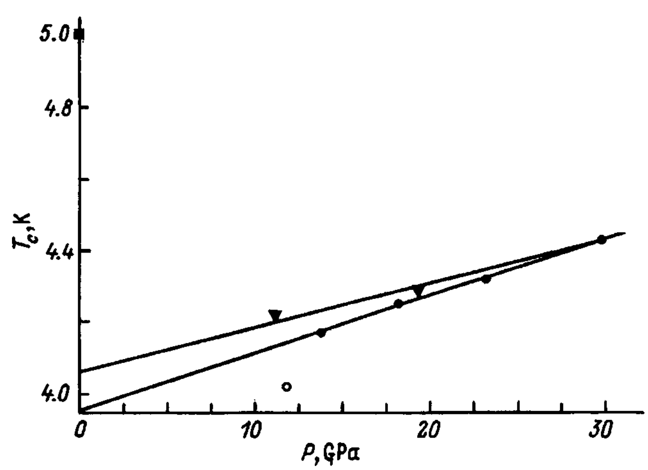

FIG. 3. Pressure dependence of the superconducting transition temperature in ζ-$TiD_{0.74}$. Transitions during loading are denoted by circles, and transitions during unloading are denoted by triangles. The initial load point probably reflects a property of an intermediate phase, and therefore is not filled in. For comparison, the superconducting transition temperature in χ-$TiD_{0.74}$ is shown by a square.[8]

formation of some intermediate phase in a relatively narrow region of the $T-P$ diagram can be another explanation of the observed deviation.

The slope of the dependence for the load curve in the region $P > 12$ GPa is $dT_c/dP = 0.016$ K/GPa, and the slope of the unloading curve is close to this value. Linear extrapolation of the $T_c(P)$ dependence to atmospheric pressure gives a value of $T_c^0 = 4.0 \pm 0.05$ K (Fig. 3), which is significantly lower than the superconducting transition temperature in the χ phase obtained after thermobaric treatment ($T_c = 5.0$ K). The entire $T_c(P)$ curve in the interval to 30 GPa lies below 4.5 K. The strong noncorrespondence of one of the main superconductivity characteristics of the χ and ζ phases agrees with the assumption expressed earlier[2,7] that it is possible that the hydrogen sublattice is reconstructed during the transition from the stability region of the ζ phase ($P \approx 5$ GPa, $T \approx 650$ K) into the region of the metastable existence of the χ phase. The set of experimental facts shown above makes it possible to discuss two mechanisms for such a reconstruction.

The chemical composition of the ζ phase corresponds to the composition of a number of possible tetragonally distorted ordered inclusion superstructures.[14] It is therefore extremely probable that the hydrogen in the high-pressure phase is ordered below a certain temperature. This transition cannot be recorded by differential thermal analysis because of kinetic or thermodynamic causes. If the hydrogen sublattice of the ζ phase is ordered under the conditions from which its quenching is carried out, reconstruction of the octahydrogen sublattice during thermobaric treatment and the return to atmospheric pressure can be the initial stage of the decay of the ζ phase as it becomes unstable; i.e., the disordering of the hydrogen can decrease the tetragonal distortion and increase the superconducting temperature in the χ phase. If, on the contrary, the hydrogen sublattice of the ζ phase is disordered for the initial parameters of the quenching, an ordered superstructure could arise during the rather slow cooling in the experiments to measure the superconductivity. The question of the possibility of ordering in the high-pressure phase can be definitively solved by a more detailed structural investigation under pressure.

Measurements of the $T_c(P)$ dependence have thus shown that the high-pressure phase in the Ti–D system is a superconductor with a transition temperature that increases from 4.17 to 4.43 K in the interval 14–30 GPa. The value of $T_c(P)$ extrapolated to atmospheric pressure is significantly below the superconducting transition temperature in the χ phase. This noncorrespondence serves as a basis for a question concerning a structural transition in the high-pressure phase, associated with the ordering of hydrogen.

The authors are grateful to V. G. Glebovskiĭ for preparing the ingot of high-purity titanium.

This work was carried out with the support of the Russian Fund for Fundamental Research in the framework of Projects No. 97-02-17614 and No. 96-15-96806.

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Translated by W. J. Manthey