Superconducting temperature of the ω-phase in Ti, Zr and Hf metals at high pressures

I.O. Bashkin *, V.G. Tissen, M.V. Nefedova, E.G. Ponyatovsky

Institute of Solid State Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow District, Russia

Abstract

The superconducting transition temperature of the Ti metal is measured in dependence on pressure to 56.0 GPa. A linear $T_c(P)$ increase is observed in the stability range of ω-Ti, like in the Zr and Hf ω-phases. This general behavior can be related to low electron density of states at the Fermi level at zero pressure and its pressure-induced increase due to the s–d electron transfer.
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At normal conditions Ti, Zr and Hf are stable in the hexagonal close-packed structure (the hcp α-phase). These three α-phases at atmospheric pressure are low-temperature superconductors with the T_c values in the range 0.25–0.50 K for α-Ti (depending on the sample pre-history), 0.45–1.1 K for α-Zr and 0.128 K for α-Hf [1–3]. Applied pressure induces a transition from the α-phase to the hexagonal ω-phase [1]. The α–ω transition is reversible in Hf [4], but does not occur in Ti and Zr on decompression at room temperature so that ω-Ti and ω-Zr remain intact at ambient conditions infinitely. At normal pressure ω-Zr is a superconductor, $T_c = 0.65$ K [2] to 0.95 K [3], but superconductivity was not observed in ω-Ti at $P = 1$ atm down to $T = 0.06$ K [3]. The pressure effect on the superconducting temperature of ω-Zr was studied in several works [5–7], and T_c was found to increase until the ω–β transition in Zr. A similar $T_c(P)$ dependence was recently observed on Hf [8].

In this work we measured the superconducting transition temperatures of titanium up to $P = 56$ GPa and found that the ω-phases of all three metals are superconductors under high pressure.

The Ti metal studied was prepared from a rod of iodide-refined Ti by means of the electron-arc zone melting in vacuum. The total impurity contents was less than 0.02 at.%. The sample was cut from a Ti chip polished to less than 0.02 mm thick.

High pressure was generated using the diamond-anvil apparatus made of non-magnetic materials [8]. The pressure-transmitting medium was the 4:1 methanol–ethanol mixture. The superconducting transitions were recorded as anomalies in the temperature dependence of the magnetic susceptibility, $\chi(T)$, measured with the alternating current of a 5.2 kHz frequency on heating the sample from the minimum temperature. The minimum temperature of about 1.3 K was obtained by vacuum pumping of the He cryostat with the high-pressure apparatus inside. The (Cu–Fe)–Cu thermocouple was used for the temperature measurements with an accuracy of ±0.2 K. Pressure was determined from the shift of the ruby luminescence line [9] after recovery of the press to room temperature at the

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* Corresponding author. Fax: +7 96 5249701.
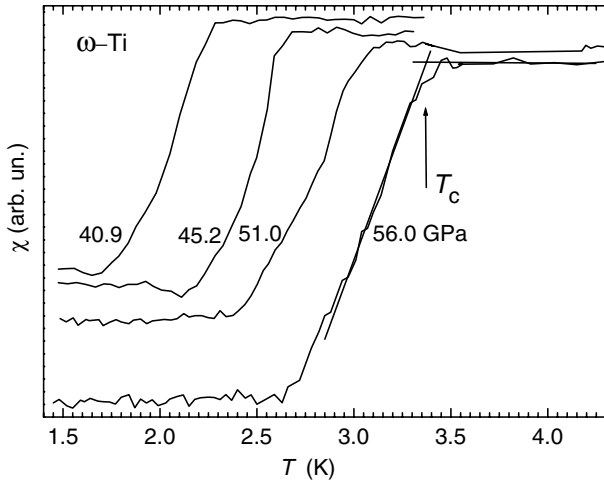*E-mail address:* bashkin@issp.ac.ru (I.O. Bashkin).

Fig. 1. Magnetic susceptibility curves, $\chi(T)$, measured on Ti at the indicated pressure values. The geometric scheme illustrates the graphical determination of T_c.

end of each cooling/heating cycle. The T_c values were determined as the intersection points between the steepest tangent to a $\chi(T)$ curve and the linear extension of the high-temperature section of the curve.

Fig. 1 presents the experimental isobars of the magnetic susceptibility measured in the stability range of ω-Ti, and Fig. 2 summarizes the experimental data in the form of the $T_c(P)$ dependence. The $T_c(P)$ data obtained for ω-Ti are also compared in Fig. 2 with similar data for ω-Zr [2,3,5–7] and ω-Hf [8].

All $T_c(P)$ dependences show a rather linear behavior in the experimental interval. A linear fit through all ω-Zr data gives a slope of $dT_c/dP = 0.115 \pm 0.01$ K/GPa and $T_c(P = 0) = 0.54 \pm 0.2$ K, which agrees with the earlier estimates [2,5]. Linear extrapolation of the ω-Hf and ω-Ti data with the slopes of $dT_c/dP \approx 0.16$ K/GPa [8] and 0.07 K/GPa, respectively, results in an intersection with the P axis at

$P \approx 26.0$ and 9.4 GPa. This correlates with the non-superconductive low-temperature behavior of ω-Ti earlier observed [3]. We note that ω-Zr and ω-Hf have approximately linear $T_c(P)$ dependences through the whole ranges of their existence up to the ω–β transition. Assuming that the $T_c(P)$ dependence for ω-Ti is also linear up to the transition to the orthorhombic γ-phase reported at about 128 GPa [10,11], the ω-Ti superconducting temperature can increase before the transition to as high value as $T_c(128) = 8.7$ K.

So, all Group IVb metals have low or zero temperatures of the superconducting transition both in α- and in ω-phases at normal pressure, but the T_c values considerably increase when pressure is applied. This behavior can be qualitatively explained on the basis of the changes in the electronic structures. It has been determined from the calorimetric measurements on many d-metals and alloys [12] that low T_c values are correlated with low electron densities of states at the Fermi level, N_F. Band-structure calculations show that applied pressure induces the s–d electron transfer in the Group IVb metals, and the estimated rate of the transfer is around 0.002 electrons/atom per GPa for α-Ti [13]. A slight increase of the d-band occupation was calculated for all Zr phases under pressure [14]. This was concomitant with the N_F increase calculated for ω-Zr at $P \approx 48$ GPa compared to that at zero pressure [14]. Similarly, calculation of the pressure effect on the properties of the equiatomic TiV and ZrNb alloys [15] resulted in the d-band occupancy increasing at a rate of 0.003–0.004 electrons/atom per GPa and a nearly linear increase in $T_c(P)$.

Another mechanism for the pressure-induced T_c increase can also be assumed that involves the enhanced electron–phonon coupling due to the low-frequency anomalies in the phonon spectra. This mechanism has been suggested recently to explain the anomalous $T_c(P)$ behavior of bcc Nb [16]. However, these kind calculations for the Group IVb metals are not available so far.
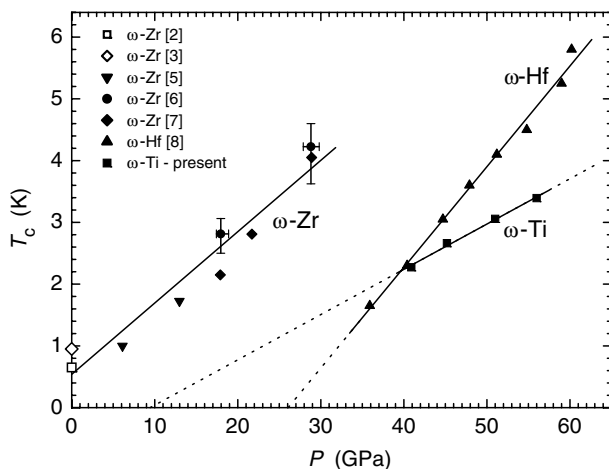
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Fig. 2. Pressure effect on the superconducting transition temperatures in Ti (black squares), Zr [2,3,5–7] and Hf [8]. Solid and dotted lines are linear fits through the experimental points and their extrapolation within the ω-phase ranges.

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