

Enhanced superconductivity of the Ti – Zr alloys in the high-pressure BCC phase

I. O. Bashkin¹⁾, V. G. Tissen, M. V. Nefedova, A. Schiwiek⁺, W. B. Holzapfel⁺, E. G. Ponyatovsky

*Institute of Solid State Physics RAS
142432 Chernogolovka, Moscow district, Russia*

⁺*Fachbereich 6 – Physik, Universität-GH Paderborn
D-33095 Paderborn, Germany*

Submitted 7 December 2000

A high-pressure study of the crystal structure and superconductivity of Ti – Zr alloys demonstrates an increase of the $\omega - \beta$ transition pressure from about 30 to 43–57 GPa when the titanium content in the alloys increases from 0 to 50 at.%. The isobaric values of the BCC β -phase superconducting temperature (at 46 GPa) increase from 5.7 to more than 15 K between 0 and 50 at.% Ti, the latter value being the absolute maximum for BCC d -metal alloys. These data correlate with the earlier assumption of an $s-d$ electron transfer in Zr under pressure.

PACS: 64.70.Kb, 74.62.-c

1. Titanium and zirconium at normal conditions are stable in the hexagonal close-packed structure (the HCP α -phase) and transform to the body-centered cubic (BCC) β -phase above 1155 and 1136 K, respectively [1]. The hexagonal ω -phase becomes stable for both metals under pressures of $P > 2$ GPa at room temperature [1–4]. Recently, Xia et al. [5] found that ω -Zr compressed to $P \approx 30$ GPa at room temperature undergoes a transition to a BCC phase which is also called β -phase, by analogy with the low-pressure / high-temperature phase. The hard-spheres packing ratio for the BCC structure is not as high as in the close packed FCC or HCP structures therefore Xia et al. related this transition to the $s-d$ electron transfer in Zr, which results in a reduction of the atomic volume [5], as discussed in theoretical studies on the relation between the crystal structure and the d -band occupancy in the non-magnetic d -band metals (see, e.g. [6–11]). Later, Akahama et al. [12] have measured the pressure dependence of the superconducting temperature, T_c , for Zr and presented new arguments for the $s-d$ electron transfer also in relation with the structural transition and with the similarity in the behavior of Zr under pressure with Group Vb metals. Actually, the T_c values increase under pressure moderately in the stability ranges of the α -Zr and ω -Zr phases, but a sharp jump by several degrees is observed near $P = 30$ GPa [12]. The idea of an electronic transition was used later in order to explain a similar $\omega - \beta$ transition in Hf around

71 GPa [13] as well as an isostructural BCC to BCC transition in Zr which was claimed to be seen at 56 GPa [14]. Titanium does not undergo a transition to the BCC phase at room temperature up to 87 GPa [13].

The hypothesis of a strong $s-d$ electron transfer for the Group IVb metals under pressure opens a door for a new study. In fact, there is a considerable difference between the Group IVb and Vb metals as well as between the binary Group IVb – Vb and Vb – Vb metal alloys with respect to their phase diagrams and superconducting properties. For example, the Ti – Zr alloys form homogeneous solid solutions both in liquid and solid states (solid α -solutions at low and moderate temperatures and β -solutions up to melting) [15]. The superconducting temperatures of pure Ti and Zr as well as of their HCP α -alloys are low and show a maximum of $T_c = 1.7$ K at the equiatomic composition, TiZr [16]. The Group Vb metals have a BCC lattice and higher T_c values ($T_c = 5.4$ and 9.26 K for V and Nb, respectively) [15, 16]. The solubility of the Group Vb metals in HCP α -Ti and α -Zr amounts only to a few percent, but the BCC alloys of the Group IVb – Vb elements are homogeneous over a much broader concentration range, e.g., the homogeneity ranges of the β -phase in the Ti – V or Ti – Nb systems at room temperature are extended from about 20 to 100 at.% V or Nb. The concentration dependence of the superconducting temperature, $T_c(x)$, in the stability range of the BCC Group IVb – Vb alloys has a maximum between 60 and 75 at.% Group Vb metal [15–18].

¹⁾e-mail: bashkin@issp.ac.ru

One can assume from this consideration that $\text{Ti}_{1-x}\text{Zr}_x$ alloys become similar to the Group IVb – Vb alloys above the high-pressure electronic transition in Zr with the respective consequences, i.e., the BCC solid solutions of titanium in β -Zr extend their stability range as the pressure is increased and the superconducting temperature increases also as the Ti content in β -Zr is increased for isobaric conditions. These assumptions are examined here by T_c measurements on Zr and its alloys with 30 and 50 at.% Ti under pressures up to the transition to the BCC phase, and the $\alpha \rightarrow \omega \rightarrow \beta$ structural sequence is confirmed by X-ray diffraction.

2. Experimental. The present alloys were prepared from the iodide Zr and Ti rods melted in vacuum by the electron arc. The purities of molten Zr and Ti were 99.96 and 99.98 at.%, respectively, the interstitial impurities taken into account. The final alloy compositions were measured by electron probe X-ray micro-analyzer JXA-5, with the results of $x = 69.3 \pm 0.8$ and $x = 50.4 \pm 0.4$ at.% Zr for the samples used in superconductivity measurements and $x = 71.9 \pm 0.8$ and $x = 50.4 \pm 0.4$ at.% Zr for the structural studies.

The superconducting transitions in the samples were registered as anomalies in the magnetic susceptibility curves, $\chi(T)$, measured with alternating current [19]. The diamond-anvil apparatus made of non-magnetic materials as well as the experimental details were described elsewhere [19,20]. Cooling of the diamond apparatus results in its mechanical relaxation and a marked pressure increase therefore pressure determination in these experiments was carried out at room temperature at the end of each experimental cooling / heating cycle. Energy dispersive X-ray diffraction (EDXD) with synchrotron radiation and diamond-anvil high-pressure cells was performed at HASYLAB (DESY, Hamburg) as described previously [21, 22].

3. Results. Typical experimental $\chi(T)$ curves for $\text{Ti}_{30}\text{Zr}_{70}$ measured on heating at constant pressures are represented in Fig.1. Similar curve shapes were characteristic for Zr and the equiatomic alloy. The jumps due to the superconducting transition are clearly visible in each curve. The jumps in most of the $\chi(T)$ isobars are very steep indicating a single-phase state of the alloy. There are, however, some pressure intervals where the superconducting $\chi(T)$ anomalies either are extended over several degrees (e.g., the 35.6 GPa isobar in Fig.1) or consist of two jumps separated by an inclined plateau (the 35.0 GPa decompression isobar in Fig.1). A strong distortion of the $\chi(T)$ anomalies is typical for pressure intervals, where the $\omega - \beta$ phase transition takes place and the alloy is in a two-phase

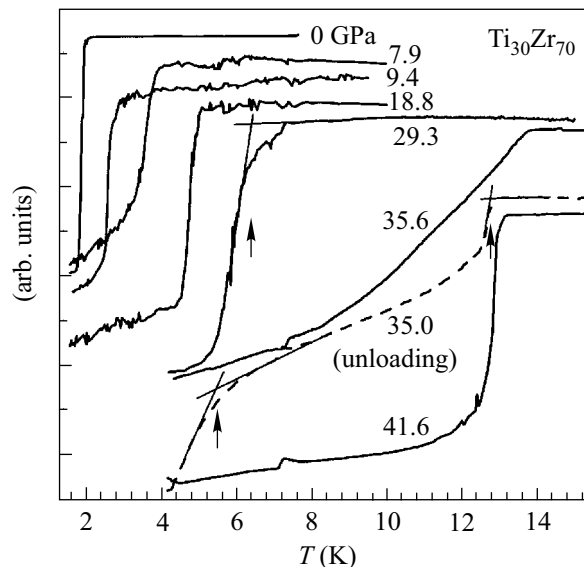


Fig.1. Representative magnetic susceptibility curves, $\chi(T)$, measured upon heating of a $\text{Ti}_{30}\text{Zr}_{70}$ alloy at indicated pressures. The arrows explain determination of the superconducting temperature from intersection of two tangents to the curve. The curves are measured in a run of stepwise compression, but for the 35.0 GPa isobar (dashed curve) measured on decompression

state. In the pressure intervals of the $\alpha - \omega$ transition, distortions of the $\chi(T)$ anomalies are rather small. The superconducting temperature was determined as the intersection point between the steepest tangent to the $\chi(T)$ curve and the linear extension of the high-temperature section of the $\chi(T)$ curve, as shown in Fig.1.

The corresponding T_c values for the three alloys are plotted versus pressure in Fig.2 together with the literature data [12, 23, 24] for pure Zr (the bottom curve). Fig.2 shows a good agreement between the different data below 30 GPa. Above this pressure, the T_c values from Akahama et al. [12] are systematically larger than the present values, probably, due to the difference in the experimental techniques: Akahama et al. [12] determined the T_c values from the resistivity measurements unlike the present $\chi(T)$ data. One can also see from Fig.2 that the $T_c(P)$ curve in the ω -Zr range is almost a smooth continuation of the $T_c(P)$ curve in the α -Zr range. The $\omega - \beta$ transition occurs in a very narrow pressure interval near 30 GPa, as reported earlier [5, 13]. After the T_c jump from 4.1 to 9.4 K due to the $\omega - \beta$ transition, further pressure increase results in a gradual decrease of T_c .

The alloys have similar $T_c(P)$ dependencies in the α - and ω -phase regions: T_c grows with increasing pressure

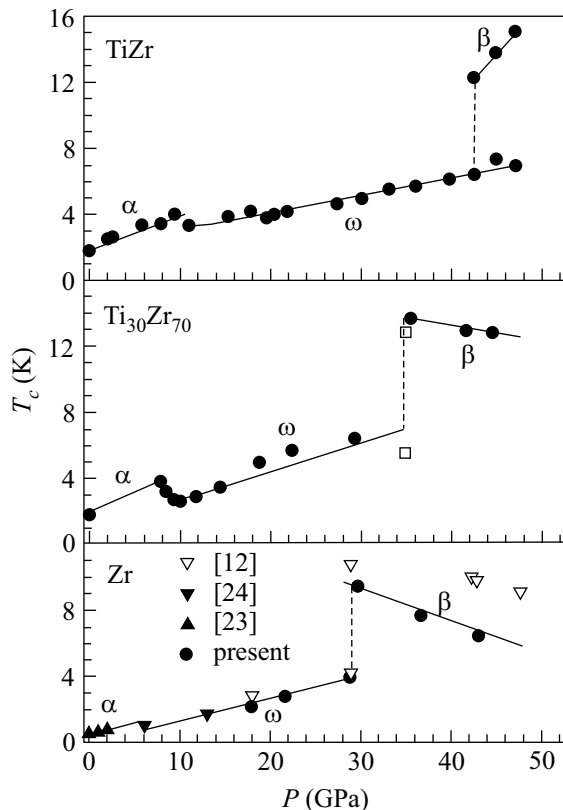


Fig.2. The pressure effect on the superconducting temperature, $T_c(P)$, for Zr (bottom), $\text{Ti}_{30}\text{Zr}_{70}$ (middle) and TiZr (top) together with literature data for Zr [12, 23, 24]. Open symbols represent data on decompression of $\text{Ti}_{30}\text{Zr}_{70}$

for both phases. Transitions to the ω -phase are observed near 10 GPa by a small but distinct decrease in T_c . The slope of the $T_c(P)$ dependence for the ω -phase of the equiatomic TiZr alloy is smaller than for the α -phase. The process of the $\omega - \beta$ transition in the alloys is different from that in pure Zr. For $\text{Ti}_{30}\text{Zr}_{70}$, the $\chi(T)$ jump is very broad around 35 GPa on increasing pressure, and two $\chi(T)$ jumps are observed in this range on decompression. This is an indication of an intermediate two-phase state occurring in an extended pressure interval. The transition hysteresis, however, remains rather small. Above the $\omega - \beta$ transition, $T_c(P)$ does not decrease as steep as in pure Zr. The two-phase nature of the $\omega - \beta$ transition is most clearly seen in the equiatomic TiZr alloy. The broad $\chi(T)$ anomaly around 40 GPa changes to two jumps at $P \geq 43$ GPa, and these two jumps are observed up to highest pressure of $P = 47$ GPa where T_c for the β -phase was 15.5 K.

The in situ EDXD measurements confirm for both alloys that the high-pressure T_c jump is related to the formation of the BCC phase. The coexistence interval of

the ω - and β -phases for the TiZr alloy is rather broad: the ω -phase is observed up to 56.3 GPa, and the alloy becomes purely β -phase at $P = 57.0$ GPa. At 47 GPa, the ω -phase is still the dominant phase of the TiZr alloy, with only about 20% β -phase. So far T_c seems to increase with pressure at least until the $\omega - \beta$ transition is completed at 57.0 GPa.

4. Discussion. The present study over a wide pressure range allowed to determine the $T_c(P)$ dependence for Zr and $\text{Ti}_{30}\text{Zr}_{70}$ in the pure β -phase. For the equiatomic alloy, the T_c value for the pure β -phase at the end of the transition should be higher than the value in the two-phase state. For the sake of comparison, Fig.3 shows the T_c values for the present alloys in the β -phase at $P = 46$ GPa in their dependence on the Zr concentration. Fig.3 shows also the earlier ambient pressure data for the β -phase Ti - V and Ti - Nb alloys [16]. From a comparison with these alloys, one could have anticipated also for the β -phase Ti - Zr alloys a small initial increase of T_c with increasing Ti content on the Zr rich side of this diagram. However, the highest observed value of $T_c = 15.5$ K for β -TiZr at 47 GPa is much higher than T_c for pure Zr as well as for any other BCC phase in the transition metal alloys.

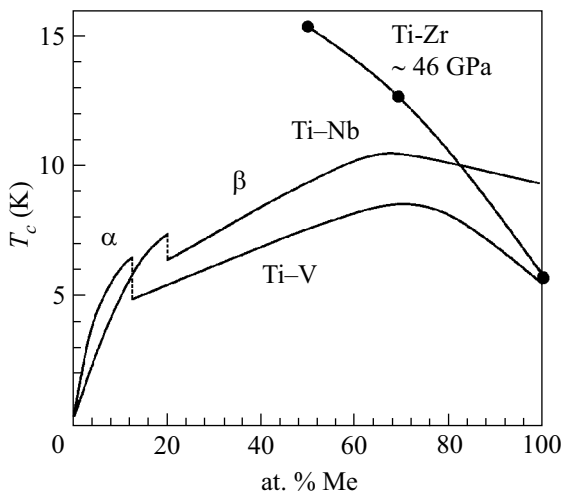


Fig.3. Effect of the concentration of the second component on the superconducting temperatures of Ti - V and Ti - Nb alloys (reproduced from ref. [16]) and for Ti - Zr alloys (at $P = 46$ GPa). For the Ti - V and Ti - Nb systems, the data in the vicinity of the α/β phase boundary were partly measured on the quenched samples [16]

The increase of T_c in the $\omega + \beta$ two-phase region of the TiZr alloy may result from proximity effects in the process of nucleation and growth of the β -phase grains.

If this is the case, the T_c values for β -TiZr should further increase until the bulk β -grains are well developed.

The T_c values increase at the ω – β transitions. Thus, the present experimental data support a correlation between the high-pressure structural ω – β transition and the expected s – d electron transfer in Zr. This observation also fits to the general assumption of a progressive s – d electron transfer in the early transition metals under pressure [6–11]. This correlation could be further elucidated by a more detailed study of $T_c(P)$ for β -TiZr at higher pressures as well as by further studies closer to the possible maximum in the isobaric $T_c(x)$ curve for the β -Ti $_{1-x}$ Zr $_x$ alloys.

The present determination of the ω – β transition pressures in the Ti $_{1-x}$ Zr $_x$ alloys at room temperature shows their strong non-linear increase with the $1 - x$ increase in the range $0 \leq 1 - x \leq 0.5$ in such a way, that the transition in pure Ti may be expected only above 100 GPa. The T_c values also increase with increasing $1 - x$ and become larger than 15 K for TiZr under pressure, which is a record for BCC transition metals and alloys. The T_c increase due to the ω – β transition is in agreement with the general assumption of a progressive s – d electron transfer in the early transition metals under pressure.

This work was supported by the RFBR Grant # 00-02-17562. HASYLAB experiments were performed under Project # II-96-76.

1. E. Yu. Tonkov, *High Pressure Phase Transformations*, Vol. 2, 1992, Philadelphia.
2. V. A. Zilbershtein, N. P. Chistotina, A. A. Zharov et al., *Fiz. Met. Metalloved.* **39**, 445 (1975).
3. F. P. Bundy, in: *New materials and Methods for Investigation of Metals and Alloys*, Moscow, 1966, p.230.
4. A. Jayaraman, W. Klement, and G. C. Kennedy, *Phys. Rev.* **131**, 644 (1963).
5. H. Xia, S. J. Duclos, A. L. Ruoff, and Y. K. Vohra, *Rhys.*

- Rev. Lett.* **64**, 6736 (1990).
6. I. V. Svechkarev and A. S. Panfilov, *Phys. Status Solidi* **b63**, 11 (1974).
7. C. Duthie and D. G. Pettifor, *Phys. Rev. Lett.* **38**, 564 (1977).
8. Y. K. Vohra, S. K. Sikka, and W. B. Holzapfel, *J. Phys. F: Metal Phys.* **13**, L107 (1983).
9. H. L. Sriver, *Phys. Rev.* **B31**, 1909 (1985).
10. M. Sigalas, D. A. Papaconstantopoulos, and N. C. Bacalis, *Phys. Rev.* **B45**, 5777 (1992).
11. R. Ahuja, J. M. Wills, B. Johansson, and O. Eriksson, *Phys. Rev.* **B48**, 16269 (1993).
12. Y. Akahama, M. Kobayashi, and H. Kawamura, *J. Phys. Soc. Japan* **59**, 3843 (1990).
13. H. Xia, G. Parthasarathy, H. Luo et al., *Rhys. Rev.* **B42**, 6736 (1990).
14. Y. Akahama, M. Kobayashi, and H. Kawamura, *J. Phys. Soc. Japan* **60**, 3211 (1991).
15. M. Hansen and K. Anderko, *Constitution of Binary Alloys*, vol. 2, New York, 1962.
16. E. M. Savitskii, Yu. V. Efimov, N. D. Kozlov et al., *Superconducting Materials*, Moscow, Nauka, 1976.
17. G. Gladstone, M. A. Jensen, and J. R. Schrieffer, *Superconductivity in the Transition Metals: Theory and Experiment*, in: *Superconductivity*, Ed. R. D. Parks, New York, 1969.
18. S. V. Vonsovskii, Yu. A. Izyumov, and E. Z. Kurmaev, *Superconductivity of Transition Metals, Their Alloys and Compounds*, Moscow, Nauka, 1977.
19. V. G. Tissen, E. G. Ponyatovskii, M. V. Nefedova et al., *J. Phys.: Condensed Matter* **8**, 3069 (1996).
20. I. O. Bashkin, M. V. Nefedova, V. G. Tissen, and E. G. Ponyatovsky, *Fiz. Tverd. Tela* **42**, 12 (2000).
21. K. Syassen and W. B. Holzapfel, *Europhys. Conf. Abstr.* **1A**, 75 (1975).
22. W. B. Holzapfel, in: *High Pressure Chemistry*, Ed. H. Kelm, Boston, 1978, p.177.
23. N. B. Brandt and N. I. Ginzburg, *Sov. Phys. Usp.* **85**, 202 (1965).
24. A. Eichler and W. Gey, *Z. Physik* **251**, 321 (1972).