Available online at www.sciencedirect.com
SCIENCE DIRECT
PHYSICA C
Physica C xxx (2006) xxx–xxx
www.elsevier.com/locate/physc

Superconducting transition temperature of the equiatomic ZrNb alloy at pressures to 56.4 GPa

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

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

Received 19 December 2005; accepted 26 December 2005

Abstract

The superconducting transition temperature of the equiatomic ZrNb alloy is measured in dependence on pressure to 56.4 GPa. The $T_c(P)$ dependence is found to achieve a maximum around 42 GPa and to have an anomalous behavior with a shallow minimum in the pressure range 5–10 GPa. This behavior of $T_c(P)$ is similar to that earlier observed on pure metal Nb. A comparison with recent model calculations suggests that the features of the $T_c(P)$ behavior both in pure Nb and in the ZrNb alloy are of the same nature and result from the high-pressure anomalies in their phonon spectra.

PACS: 74.62.Fj

Keywords: Superconducting transition temperature; High-pressure; ZrNb alloy

The electronic band structure calculations rather early resulted in a conclusion on the pressure-induced transfer of the s-electrons to the d-band in the metals opening the series of the periodic table [1,2]. As the accuracy of the model calculations increased, the pressure dependence of the band structure and the properties of metals as well as a correlation between the band structure and the stability of the crystal lattice have been a subject of many works.

Transitions to the body-centered cubic phase in zirconium and hafnium under pressure have also been related to the s → d electron transfer [3–5]. Formation of the bcc phase in Zr [6] and Hf [7] is concomitant with an abrupt increase of the superconducting transition temperature, T_c. Akahama et al. [8] noticed that the bcc β-Zr phase formed at $P = 30$ GPa had approximately the same values of the specific volume and T_c as bcc Nb at atmospheric pressure. They assumed therefore that the Group IV metal, Zr, becomes a close analogue of the Group V metal, Nb, due to increasing occupancy of the d-band on compression. The experimental data on the high-pressure behavior of the crystal structure and the superconducting temperature of the Zr–Ti [9,10] and Zr–Hf [11] alloys were also discussed in relation to the s → d transfer in Zr and Hf under pressure.

These speculations, however, are not well supported by the theoretical estimate of the s → d transfer in Zr [5] indicating that the number of the electrons transferred in the relevant pressure range is considerably less than unity for all phases. A correlation between the number of the electrons transferred and T_c was not theoretically considered for the Group IV metals as well as for their alloys until recently. The first estimation of this kind was given for the equiatomic bcc ZrNb and TiV alloys whose band structure, the d-band occupancy and T_c were calculated at several pressure values [12]. The calculation based on few experimental points measured on ZrNb in a pressure range limited to 25 GPa [13] therefore a more detailed experimental test of the correlation between the actual and estimated T_c values in a broader pressure range was of interest. Further, accurate data for bcc ZrNb was expected to extend the experimental basis for conclusions on the $T_c(P)$ behavior of other related bcc phases.

* Corresponding author. Fax: +7 096 5249701.
E-mail address: bashkin@issp.ac.ru (I.O. Bashkin).

0921-4534/$ - see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.physc.2005.12.065

This work presents the $T_c(P)$ dependence of the bcc ZrNb alloy measured up to $P = 56.4$ GPa and compared to the available model calculations.

To prepare the ZrNb alloy, initial Zr and Nb metals of 99.95 at.% purity were cut to chips, mixed up and compacted to a cylindrical ingot that was subjected to multiple electron-arc melting in vacuum. The final composition of the alloy was tested using the JXA-5 local X-ray microanalyzer, it was stoichiometric within the experimental accuracy of ±1 at.%. The bcc single-phase state of the alloy was checked using the X-ray diffraction.

High-pressure was generated with a diamond-anvil cell. The pressure-transmitting medium was the 4:1 methanol–ethanol mixture. The superconducting transitions were recorded as jumps in the thermal dependence of the magnetic susceptibility, $\chi(T)$, measured on heating. To eliminate the effects due to the mechanical relaxation of the press upon cooling to helium, the pressure was determined from the shift of the ruby luminescence line after recovery of the press to room temperature at the end of the cooling/heating cycle. Other details of the device and the experimental procedure are described elsewhere [7,10].

The measured T_c values are plotted in dependence on pressure in Fig. 1 (black circles). The T_c values are determined from the experimental $\chi(T)$ curves as intersection points between the steepest tangent to the curve and the linear extension of the high-temperature section of the curve, as illustrated in the inset. The widths of the superconducting transitions are about 0.5 K at low pressures and increase twice at highest pressures. The prominent features of the $T_c(P)$ curve are a drastic decrease of the slope in a narrow pressure interval of 5–10 GPa and a broad maximum around $P = 42$ GPa. Above the maximum, $T_c(P)$ is decreasing with increasing pressure.

Earlier data measured on a nearly stoichiometric Zr–Nb alloy in the range to 25 GPa [13] are shown in Fig. 1 in open circles. The agreement between the present and earlier data is mainly quantitative, but the low-pressure $T_c(P)$ anomaly was not found by Kawamura et al. [13]. This seems to be due to scanty experimental points in the relevant pressure interval in Ref. [13]. The dotted line in Fig. 1 is drawn through the calculated T_c values (crosses) presented in Table 3 of Ref. [12], the dashed line represents the pressure dependence of the d-band occupancy, N_d, of the ZrNb alloy taken as the average of the d-electron numbers listed for the constituent Zr and Nb atoms in Table 1 [12]. One can see from Fig. 1 that the calculated $T_c(P)$ and $N_d(P)$ dependencies demonstrate an approximately linear increase with pressure. The only deflection from a smooth dependence is the T_c value calculated at $P = 21.72$ GPa; this deflection was not discussed in Ref. [12]. On the basis of this relationship between T_c and N_d, Selvamany et al. [12] concluded that the continuous increase in T_c of the ZrNb alloy is related to the continuous electron transfer from the sp-states to the d-states. To support this conclusion, Selvamany et al. [12] indicated that both the s–d electron transfer and the T_c increase in the ZrNb alloy under pressure are more rapid than in the TiV analogue.

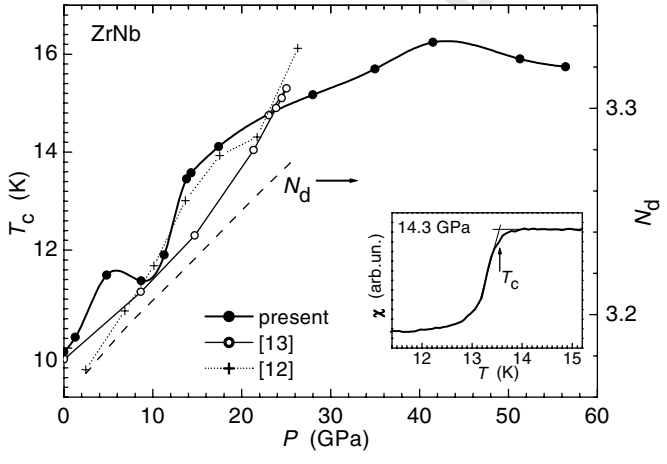

Fig. 1. Pressure effect on the superconducting transition temperature in the ZrNb alloy (black circles). Open circles are for the earlier data to 25 GPa [13]. Calculated data [12] are shown with crosses and the dotted line. The dashed line is for the d-band occupancy, N_d (right axis). Determination of the T_c values from the $\chi(T)$ curves is illustrated for the 14.3 GPa isobar.

A comparison of the calculated and present data shows their proximity in the pressure range 8–25 GPa, but the experimental $T_c(P)$ curve as a whole has a more complex shape. The calculation does not reproduce a distinct anomaly at 5–13 GPa in the experimental curve resulting in a shallow minimum near $P = 10$ GPa. We do not think that the lacking anomaly in the calculated data [12] is due to a usual simplifying assumption that the ZrNb alloy is an atomically ordered bcc phase whereas the actual Zr–Nb alloys are disordered solid solutions; rather this is due to insufficient accuracy of the calculation. Finally, calculation [12] is limited to $P = 26.29$ GPa therefore it is not clear whether this calculation method can reproduce the high-pressure $T_c(P)$ maximum.

Further insight into the $T_c(P)$ behavior of the ZrNb alloy can be achieved from comparison with the experimental and theoretical data obtained for pure Nb [14–17]. The experimental $T_c(P)$ curve for Nb has similar features, i.e., a distinct shallow minimum at pressures around 5 GPa and decreasing $T_c(P)$ above $P = 60$ GPa [14]. Struzhkin et al. [14] suggested that these anomalies arose from changes in the Fermi surface topology at 5 and 60–70 GPa. Subsequent theoretical works [15–17] presented calculation of the band structure of Nb at atmospheric and high pressures in order to explain the anomalous superconducting behavior. All three calculations reported no marked changes in the Fermi surface topology below 40–50 GPa and an essential change in the topology at higher pressures. The latter effect was related to the decreasing $T_c(P)$ behavior above 60 GPa in Refs. [15,16]. The $T_c(P)$ anomaly around 5 GPa either remained unexplained [15] or was attributed to very subtle changes in the topology of the Fermi surface [16]. Wierzbowska et al. [17] supplemented the band structure calculation with calculation of the phonon spectra of Nb. They found that the phonon spectra had an anomalous pressure

dependence: low-frequency phonon peaks close to the Γ-point of the Brillouin zone (Kohn anomalies) were observed in some pressure range below 60 GPa, and the phonon linewidths increased for some modes in the same pressure interval. The occurrence of the Kohn anomalies is connected with the increase of the electron–phonon coupling constant and the T_c values in the pressure range 5–60 GPa [17]. This interpretation is rather uncommon; it can also explain the high-pressure superconducting behavior of the ZrNb alloy. So far as the phonon spectrum is determined primarily by the bcc lattice, one may think that the spectrum anomalies similar to those found in Ref. [17] also occur if the electron concentration is somewhat varied by alloying. It is expected therefore that the $T_c(P)$ dependence of many bcc Zr–Nb alloys and, probably, of the virtual bcc Zr phase in the range of its instability at $P < 30$ GPa is a curve with a maximum below 60 GPa and an anomaly at markedly lower pressures. So, the Zr–Nb system where the electron concentration and the position of the Fermi level with respect to the d-band features are readily varied by a change of the alloy composition is a convenient test for the present-day models dealing with the effect of the electron band structure, the d-band occupancy and the phonon spectrum on the superconducting transition temperature.

Acknowledgements

This work was supported by the RFBR Grant No. 03-02-17005 and by the RAS program "Thermal physics and mechanics of the intense impulse effects".

References

[1] G.M. Gandelman, V.M. Ermachenko, Ya.B. Zeldovich, Zh. Exp. Theor. Phys. 44 (1963) 386.
[2] J.C. Duthie, D.G. Pettifor, Phys. Rev. Lett. 38 (1977) 564.
[3] H. Xia, S.J. Duclos, A.L. Ruoff, Y.K. Vohra, Phys. Rev. Lett. 64 (1990) 204.
[4] H. Xia, A.L. Ruoff, Y.K. Vohra, Phys. Rev. B 44 (1991) 10374.
[5] R. Ahuja, J.M. Wills, B. Johansson, O. Eriksson, Phys. Rev. B 48 (1993) 16269.
[6] Y. Akahama, M. Kobayashi, H. Kawamura, J. Phys. Soc. Japan 59 (1990) 3843.
[7] I.O. Bashkin, M.V. Nefedova, V.G. Tissen, E.G. Ponyatovsky, JETP Lett. 80 (2004) 655.
[8] Y. Akahama, M. Kobayashi, H. Kawamura, J. Phys. Soc. Japan 60 (1991) 3211.
[9] I.O. Bashkin, V.G. Tissen, M.V. Nefedova, A. Schiwek, W.B. Holzapfel, E.G. Ponyatovsky, JETP Lett. 73 (2001) 75.
[10] I.O. Bashkin, V.K. Fedotov, M.V. Nefedova, V.G. Tissen, E.G. Ponyatovsky, A. Schiwek, W.B. Holzapfel, Phys. Rev. B 68 (2003) 054401.
[11] I.O. Bashkin, M.V. Nefedova, E.G. Ponyatovsky, V.G. Tissen, JETP Lett. 78 (2003) 80.
[12] P. Selvamani, G. Vaitheeswaran, V. Kanchana, M. Rajagopalan, Physica C 370 (2002) 108.
[13] H. Kawamura, J. Wittig, B. Bireckoven, W. Buckel, Physica B 126 (1984) 485.
[14] V.V. Struzhkin, Y.A. Timofeev, R.J. Hemley, H.K. Mao, Phys. Rev. Lett. 79 (1997) 4262.
[15] S.F. Ostanin, V.Yu. Trubitsin, S.Yu. Savrasov, M. Alouani, H. Dreyssé, Comp. Mater. Sci. 17 (2000) 202.
[16] J.S. Tse, Z. Li, K. Uehara, Y. Ma, R. Ahuja, Phys. Rev. B 69 (2004) 132101.
[17] M. Wierzbowska, S. Gironcoli, P. Giannozzi, <cond-mat/0504077>.