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Superconducting Transition Temperature in Hafnium under Pressures up to 64 GPa

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The superconducting transition temperature T_c of hafnium is measured as a function of pressure up to 64 GPa. The character of the pressure dependence of T_c observed at α–ω–β transitions in Hf is found to be similar to that observed for Zr. In the regions of α and β phases, T_c increases with pressure with the slopes $dT_c/dP = 0.05$ and 0.16 K/GPa, respectively. At the α–ω transition, $T_c(P)$ exhibits a tendency to a decrease, while at the ω–β transition, T_c increases stepwise from 5.8 to 8.0 K. The α–ω transition occurs at pressures between 31.2 and 35.9 GPa, and the ω–β transition, at a pressure of 62 ± 2 GPa. *© 2004 MAIK "Nauka/Interperiodica".*

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1. INTRODUCTION

Under normal conditions, the group IV transition metals Ti, Zr, and Hf have a hexagonal close-packed structure (the hcp α phase), whereas, under pressure, all three elements undergo polymorphic transitions [1]. Titanium first transforms to the hexagonal ω phase and then, under $P \leq 116$ GPa, to the γ and δ phases with orthorhombic structures [2, 3]. The α–ω–β series of structural transitions including the bcc β phase was first observed for Zr [4] and later, for Hf [5]. For Zr, the pressure corresponding to the ω–β transition lies within 30 [6] to 33 GPa [4]; for Hf, this pressure was found to be $P = 71$ GPa [5]. A correct description of the α–ω–β transition series was obtained as a result of theoretical calculations of the structural stability under pressure [7–9], which attributed the structural changes to the *s*–*d* electron transfer and the corresponding increase in the *d* band population. The measurements of the superconducting transition temperature T_c under pressures up to 48 GPa revealed a stepwise increase in T_c at the ω–β transition in zirconium [10]. Akahama *et al.* [6] noted the closeness of the temperature T_c and the specific volume of bcc niobium under atmospheric pressure to the respective values obtained for β-Zr under $P = 30$ GPa. These facts were explained by an increase in the *d* band population to a value typical of the group V elements.

Later, structural measurements and measurements of T_c under pressure were carried out for a number of Zr–Ti [11, 12] and Zr–Hf [13] binary alloys. In all the alloys studied, T_c also increased stepwise at the ω–β transition. The isobaric dependences of T_c on the alloy composition, which were obtained from high-pressure experimental data, had a dome like shape similar to that of the corresponding curves obtained for group IV–V alloys at atmospheric pressure [14].

In the framework of the concept of interband electron transfer under pressure, the similarity between the behaviors of Zr and Hf structures under pressure suggests that the pressure dependence of T_c for Hf should be similar to that previously observed for Zr. However, the dependence of T_c on pressure up to the ω–β transition has never been studied experimentally for Hf. In this paper, we describe the measurements of the dependence of T_c on pressure up to 64 GPa for hafnium. In the experimental dependence $T_c(P)$, we reveal anomalies and attribute them to the α–ω–β structural transitions.

2. EXPERIMENT

The metallic Hf used in the experiment was prepared by the zone melting of an iodide Hf bar in vacuum. The purity of the initial metal was no lower than 99.95 at. % with allowance for interstitial impurities. The samples were made by grinding chips of the initial metal to a thickness of ~0.02 mm.

High pressures were obtained using a diamond anvil system made of nonmagnetic materials [15]. The measuring cell is shown in Fig. 1 (the scales are approximately retained). The measuring coil was mounted symmetrically around the anvils, and the reference coil lay in the same plane with the measuring one, at a distance of about 1 mm. The secondary coils were connected against each other. The diameter of the working area of the anvils was about 0.4 mm. The sample and the reference ruby crystals were placed between the anvils in the opening of a metal gasket 0.12 mm in diameter. The pressure medium was a 4 : 1 methanol–ethanol mixture. The pressure was determined by the displacement of the ruby luminescence line with an accuracy of ±0.05 GPa after low-temperature measure-

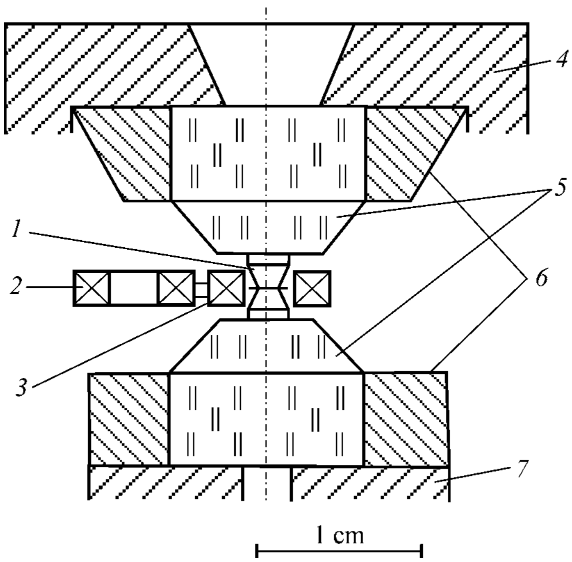

Fig. 1. Pressure cell of the diamond anvil system: (*1*) diamond anvils, (*2*) reference coil, (*3*) measuring coil, (*4*) cylinder of the press, (*5*) sapphire supports, (*6*) supporting rings, and (*7*) piston of the press.

ment cycles with the subsequent heating of the press to room temperature.

The superconducting transitions were detected as anomalies in the temperature dependence of magnetic susceptibility $\chi(T)$, which was measured with a 5.2-kHz alternating current as the sample was heated from the minimum temperature. The minimum temperature equal to 1.3 K was achieved by the vacuum pumping of helium from the cryostat containing the high-pressure system. The temperature was measured with an accuracy of ±0.2 K by a (Cu–Fe)–Cu thermocouple.

The T_c values were determined as the intersection points of the tangent to the steeply dropping part of the $\chi(T)$ curve and the extension of its high-temperature horizontal part.

3. RESULTS

Figure 2 shows typical magnetic susceptibility curves $\chi(T)$ measured by heating the sample in different pressure intervals, and Fig. 3 represents the experimental data as the dependence $T_c(P)$.

At atmospheric pressure, Hf has T_c = 0.128 K [1], which is far below the limit of our measurements. For the first time, the anomaly arising in the $\chi(T)$ curve at the beginning of the superconducting transition was observed at a pressure of 31.2 GPa. At the next pressure value of 35.9 GPa, the superconducting transition also occurred near the lower boundary of the measurement range. In the pressure interval P = 40–60.2 GPa, both the beginning and the end of the superconducting transition could be detected in the $\chi(T)$ curves. For all the pressures within this interval, the superconducting transition was spread in temperature over ~1 K. In the pressure interval from 35.9 to 60.2 GPa, the transition points determined as indicated above proved to lie on a single straight line within the measurement accuracy (Fig. 3), and the slope of this line was $dT_c/dP = 0.16 \pm 0.01$ K/GPa. According to the x-ray structural data [5], the α–ω transition in Hf occurs within 38 ± 8 GPa. Hence, the linear dependence in the interval of 35.9–60.2 GPa reflects the behavior of the superconducting transition temperature in ω-Hf. The point determined at 31.2 GPa lies far from this dependence and, presumably, represents the higher temperature of the superconducting transition in α-Hf. In this case, for α-Hf, the slope is $dT_c/dP \approx 0.05$ K/GPa. According to Fig. 3, the

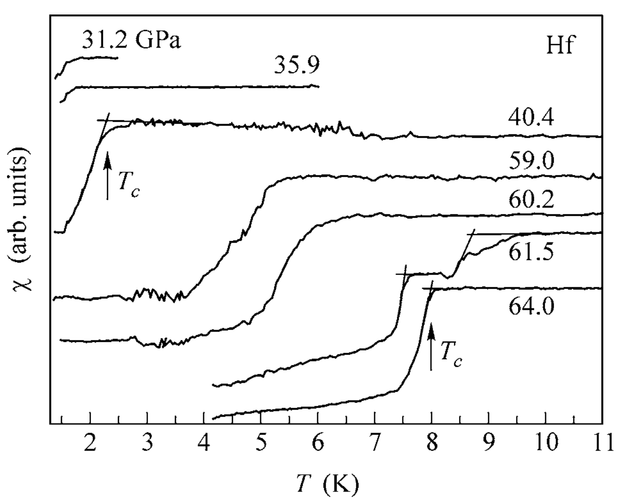

Fig. 2. Magnetic susceptibility curves $\chi(T)$ measured by heating the sample under the different pressures indicated in the plot. The straight lines illustrate the graphical determination of T_c.

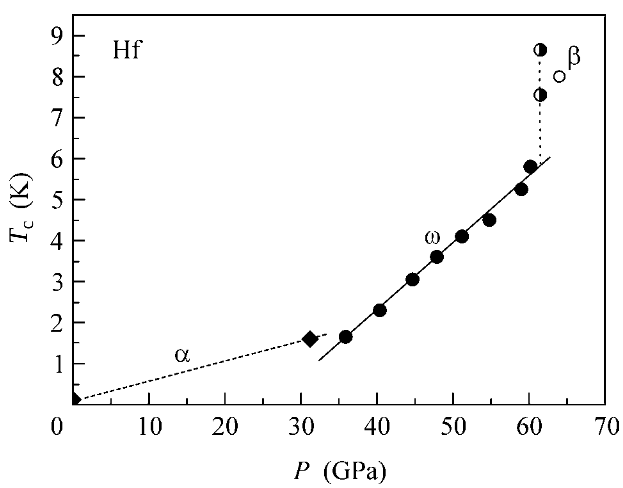

Fig. 3. Pressure dependence of the superconducting transition temperature for Hf. The different kinds of points refer to different phase states of Hf (see the body of the paper).

α–ω structural transformation occurs in Hf between 31.2 and 35.9 GPa. Thus, the pressure and the interval of the α–ω transition that we observed in Hf are noticeably smaller than those obtained from structure studies [5], but the narrow interval of this transition agrees well with the data obtained for Zr [4, 6, 10] and for Zr–Ti and Zr–Hf alloys [11–13].

Under higher pressures, the anomaly of $\chi(T)$ changes. The two-step shape of the jump in $\chi(T)$, which is observed at P = 61.5 GPa in Fig. 2 at T_c = 7.55 and 8.65 K, is an indication of a two-phase ω + β state of the sample under these conditions. The next measurement at P = 64.0 GPa revealed an abrupt jump of $\chi(T)$ at T_c = 8.0 K within an interval smaller than 0.5 K. The latter value of T_c lies far above the linear dependence $dT_c(P)$ obtained for ω-Hf and indicates a transition to a new single-phase state of Hf, i.e., to the β phase. The fracture of the pressure cell did not allow us to study the behavior of T_c in the β-Hf stability region.

4. CONCLUSIONS

The α–ω–β structural transitions in Hf are accompanied by changes in T_c, which are similar to those observed in Zr and in Zr–Ti and Zr–Hf alloys. In the regions of stability of the α and ω phases of Hf, the superconducting transition temperatures increase with pressure. The α–ω transition is presumably accompanied by a small decrease in T_c, whereas the ω–β transition is accompanied by a stepwise increase in T_c from 5.8 to 8.0 K.

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