Temperature dependence of the ω-bcc phase transition in zirconium metal

Hui Xia, Arthur L. Ruoff, and Yogesh K. Vohra

Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853

(Received 11 June 1991)

High-pressure, high-temperature energy-dispersive x-ray diffraction studies were carried out on the group-IV transition-metal zirconium (Zr) to 36 GPa using a synchrotron-radiation source to investigate the entropy contribution in the ω-to-bcc phase transition. A room-temperature equilibrium transformation pressure of 35 ± 3 GPa between the ω and bcc phases of Zr metal was observed. A negative slope of 39 ± 5 K/GPa along the ω-bcc phase boundary observed in this experiment gives experimental evidence indicating thermal contribution to the structural sequences in transition metals and shows that the ω phase of Zr metal (a phase of group-IV transition metals) has lower entropy than its pressure-induced bcc phase (isostructural with group-V transition metals). Extrapolation of the present data indicates that the previous observation of a phase transition in shock-wave experiments at 26 GPa and 540 K is due to this ω-to-bcc phase transition.

Many elemental metals tend to have certain crystal structural sequences when viewed as functions of atomic number. The most prominent example of this phenomenon is the d transition metals (as shown in Table I). Similar transition-metal structural sequences are also expected to occur in individual transition metals with increasing pressure since compression leads to an increase in d-electron population by transfer of electrons from the s band. These pressure-induced phase transformation sequences have received extensive experimental as well as theoretical attention. The room-temperature hcp-ω-bcc structural sequence had been studied in group-IV transition metals Zr, Ti, and Hf.[1-4] Calculations of the crystal structures using first-principles theory,[5,6] which is based on one-electron approximation of e-e correlation and linear-muffin-tin orbital (LMTO) calculations of total internal crystal energy versus volume $E(V)$, were generally considered to be successful in explaining the structural sequences in transition metals. However, in this theory, the energy contribution from electronic structure, especially from d electrons, plays a critical role in determining crystal structures of these transition metals and the entropy contribution to the structural sequence is generally neglected. A theoretical calculation on the bcc phase of Ti metal at room pressure has been done by Petry *et al.*[7] based on the phonon-dispersion calculation of the bcc Ti structure. Their calculation gives the vibrational entropy difference of about $0.29k_B$/atom between the ω and bcc phases of Ti. It will be of interest to make an experimental investigation on this thermal contribution to these structural sequences. A quick approach to this investigation is a high-pressure, high-temperature study near the room-temperature ω-bcc phase transformation pressures of these transition metals.

In this paper the experimental results of high-pressure, high-temperature study of a group-IV transition metal Zr will be presented. Zirconium metal is known to crystallize in a hcp structure (α phase) at ambient conditions, and transform to a bcc structure (β phase) above 1135 K at atmospheric pressure. Also, a phase transformation from the hcp phase to an ω hexagonal structure (ω phase) with equilibrium transition pressure of 2.2 GPa is known to occur at room temperature.[1] Jayaraman *et al.* measured the slope of various phase boundaries at high temperature and high pressure up to 6.5 GPa and located the triple point in the phase diagram of Zr.[8] The room-temperature x-ray-diffraction data of the Zr sample presented here show a structural phase transition at a pressure of 35 ± 5 GPa from the ω phase to a bcc phase. This value is slightly higher than the equilibrium pressure of 30 GPa reported earlier.[2] We believe that this discrepancy is due to the pressure gradient in a large gold marker employed in the previous work. This room-temperature ω-bcc phase transformation pressure is in qualitative agreement with the theoretical estimation by Gyanchandani *et al.*,[9] based on the LMTO method, though the theoretical transition pressure of 15 GPa is lower than the experimental value. High-temperature x-ray-diffraction studies of Zr metal show a negative slope of 39 ± 5 K/GPa and a large hysteresis with temperature along the ω-bcc phase boundary of Zr metal, which gives experimental evidence of the thermal contribution to the structural sequence in the transition metal Zr and indicates that the ω phase of Zr metal has higher entropy than in its pressure-induced bcc structure (a structure of a group-V transition metal). This high-temperature phase-transition result is in qualitative agreement with previous shock-wave data[10] of 26 GPa and 540 K by extrapolation of the phase boundary with this negative slope.

Details of the experimental apparatus and techniques of

TABLE I. Structural sequences of transition metals viewed as a function of their atomic numbers (or as a function of their d-band occupancies).

Period N	3	4	5	6	7	8	9	10	11
$3d,4s$	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
$4d,5s$	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag
$5d,6s$	[La]	Hf	Ta	W	Re	Os	Ir	Pt	Au
	hcp		bcc		hcp			fcc	

this high-pressure, high-temperature study can be found in Ref. 11. A high-pressure cell with diamond-anvil tips 300 μm in diameter and a sample region 75 μm in diameter was used in this experiment. Several pieces of 25-μm-thick Zr foil with a purity of 99.996% were placed in a sample region of 75 μm in diameter. A small piece of ruby chip was placed on top of the sample chamber for pressure calibration at room temperature. Gold powder was also employed as an internal pressure marker. The sample pressure at high temperature was determined by x-ray diffraction of the tiny amount of gold powder spread over the sample region. The isothermal equation of the state of gold was measured by Jamieson et al. [12] and Heinz et al. [13] The difference between their results is less than 1 GPa in the pressure and temperature ranges of this experiment. Temperature correction of the equation of the state of gold was estimated to be within ± 1 GPa.

The Zr sample was preloaded to a pressure of 32 GPa and x-ray-diffraction data at this pressure showed that the sample was in the ω phase. The Zr metal remained in the ω phase as the sample was heated to 393 K and transformed into a bcc phase at a temperature of 448 K. Figures 1(a) and 1(b) show the highly energy-dispersive x-ray-diffraction patterns of Zr and Au (as a pressure marker) at temperature of 343 and 448 K, respectively, during the heating. The sample transformed back to the ω phase when temperature was cooled down to 348 K [Fig. 1(c)]. It is known that a bcc structure can be obtained by splitting of the alternating (001) plane along the c axis of an ω

structure into two (111) planes of the bcc phase. Therefore, the x-ray-diffraction spectrum of the ω phase contains all the diffraction lines of the bcc phase and some additional diffraction lines resulting from its superlattice structure. In agreement with the above statement, this phase transition is characterized by the disappearance of superlattice diffraction lines [(111), (002), (112), and (031)] of the ω phase [Fig. 1(b)] when the sample was heated and the reappearance of these superlattice diffraction lines when the sample was cooled [Fig. 1(c)]. The temperature dependence of the equation of the state of gold metal is given in Refs. 12 and 13. The correction to the pressure is within 1 GPa for pressure below 36 GPa and temperature below 600 K. The amount of alloying of the Zr and Au metals can be neglected in this temperature range and period of time.

This temperature-induced structural phase transformation of Zr metal was measured at several pressure points. A negative slope of 39 ± 5 K/GPa along the ω-bcc phase boundary, and an equilibrium transition pressure of 35 ± 5 GPa at room temperature were observed in the Zr sample. Based on the previous compilation of equilibrium phase diagrams of the group-IV transition metals,[14] the bcc phase is a high-temperature phase with a positive slope dT/dP of 6 K/GPa along the ω-bcc phase boundary near the triple points of the hcp-ω-bcc phase diagram. The observation of the bcc phase at room temperature and high pressure in the previous experiment[2] and this experiment indicate that the high-temperature phase can also be obtained purely by an application of pressure. From this phase diagram we can also suggest that the previous shock-wave result showing a phase transition at 26 GPa and 540 K is due to this ω-bcc phase transformation and
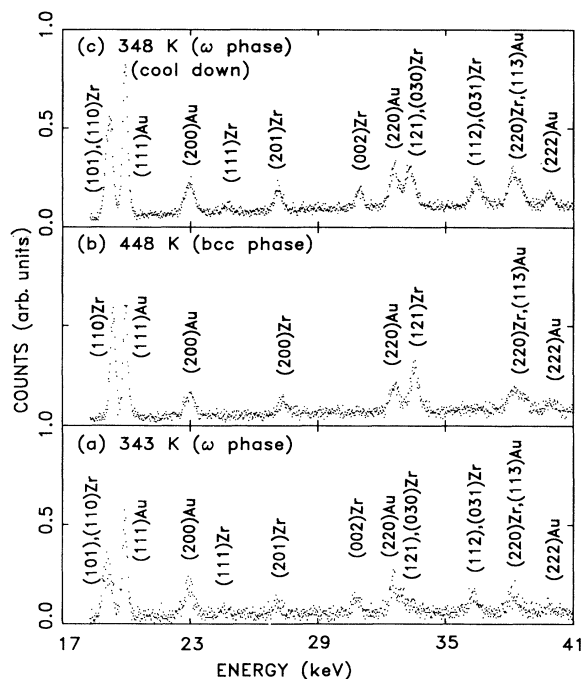

FIG. 1. Energy-dispersive x-ray-diffraction spectra of the Zr sample at various temperatures and 32 GPa (Ed =44.962 ± 0.007). (a) ω phase at 343 K during increasing of the temperature. (b) bcc phase at 448 K during increasing of the temperature. (c) Reversal of transformation at 348 K during decreasing of the temperature.
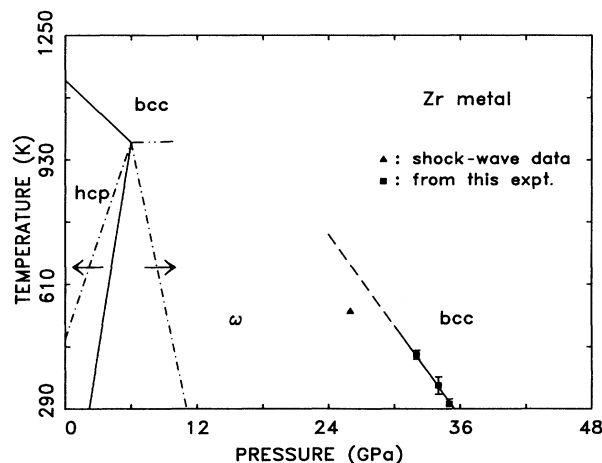

FIG. 2. The phase diagram of Zr metal for the three phases: α (hcp); ω (omega-hexagonal); and β (bcc). A negative slope of 39 ± 5 K/GPa along the ω-bcc phase boundary, and an equilibrium transition pressure of 35 ± 5 GPa at room temperature were observed in the Zr sample. From this phase diagram we can also explain that the previous shock-wave result of a phase transition at 26 GPa and 540 K is due to this ω-bcc phase transformation. Besides the data points from this experiment and shock-wave result, other curves are from the phase diagram compiled by Kutsar (Ref. 13).

the high-pressure and high-temperature stability fields of the bcc phase are probably connected. Figure 2 shows the phase diagram of Zr metal at high pressure and high temperature.

According to the previous experiment of Zr metal,[2] there is a volume decrease of about 1.6% during the ω-to-bcc phase transition at room temperature. Based on the Clausius-Clapeyron equation of a first-order phase transition

$$\frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1} , \tag{1}$$

and using the negative slope dT/dP of 39 ± 5 K/GPa measured in this experiment, we can get 1.1 cal/K mol or $0.55 k_B$/atom of increase in entropy during the ω-to-bcc phase transformation of Zr metal near room temperature. This implies that Zr metal has higher phonon density of states in its bcc phase than in its ω phase which may be due to the open structure of the bcc phase.

The observation of the negative slope of the ω-bcc phase boundary of 39 ± 5 K/GPa gives experimental evidence of thermal (entropy) contribution (about 1.1 cal/K mol or $0.55 k_B$/atom) to the structural sequence in transition metals and indicates that the ω phase of Zr metal (a phase of group-IV transition metals) has lower entropy than in its pressure induced bcc phase (isostructural with group-V transition metals). It also indicates that the previous observation of a phase transition in shock-wave experiments is due to this ω-to-bcc phase transition at high temperature and we can expect that the high-pressure and high-temperature stability fields of the bcc phase are connected. The hysteresis with temperature during the transformation was also observed in this experiment. The room-temperature x-ray-diffraction data of the Zr sample obtained in this experiment show the ω-to-bcc structural phase-transition pressure of 35 ± 5 GPa. We expect that other group-IV transition metals Ti and Hf have similar phase diagrams. We also expect that, with the current multimegabar pressure capability of diamond-anvil cells,[15,16] pressure-induced structural sequences and high-pressure, high-temperature phase diagrams may be experimentally studied for the transition metals near the middle of the transition element series. Theoretical calculations about the entropy contribution to the structural sequences in transition metals will be needed to quantitatively explain the experimental results.

[1]S. K. Sikka, Y. K. Vohra, and R. Chidambaram, Prog. Mater. Sci. **27**, 245 (1982).

[2]Hui Xia, Steven J. Duclos, Arthur L. Ruoff, and Yogesh K. Vohra, Phys. Rev. Lett. **64**, 204 (1990).

[3]Hui Xia, Steven J. Duclos, Arthur L. Ruoff, and Yogesh K. Vohra, Mod. Phys. Lett. B **4**, 585 (1990).

[4]Hui Xia, G. Parthasarathy, Huan Luo, Yogesh K. Vohra, and Arthur L. Ruoff, Phys. Rev. B **42**, 6736 (1990).

[5]A. K. McMahan, Physica **139 & 140B**, 31 (1986).

[6]Hans L. Skriver, Phys. Rev. B **31**, 1909 (1985).

[7]W. Petry, A. Heiming, J. Trampenau, M. Alba, C. Herzig, H. R. Schober, and G. Vogl, Phys. Rev. B **43**, 10 933 (1991).

[8]A. Jayaraman, W. Klement, Jr., and G. C. Kennedy, Phys. Rev. B **131**, 644 (1963).

[9]J. S. Gyanchandani, S. C. Gupta, S. K. Sikka, and R. Chidambaram, in *International Conference on High Pressure Science and Technology, Paderborn, West Germany, 1989*, edited by W. B. Holzapfel *et al.* (Gordon and Breach, New York, 1990), p. 472.

[10]R. G. McQueen, S. P. Marsh, J. W. Taylor, J. N. Fritz, and W. J. Carter, in *High Velocity Impact Phenomenon*, edited by R. Kinslow (Academic, New York, 1970), p. 537.

[11]Hui Xia, Ph.D. thesis, Cornell University, 1990 (unpublished).

[12]J. C. Jamieson, J. N. Fritz, and M. H. Manghnani, Adv. Earth Planet. Sci. **12**, 27 (1980).

[13]D. L. Heinz and R. Jeanloz, J. Appl. Phys. **55**, 883 (1984).

[14]A. R. Kutsar, Fiz. Metal. Metalloved **39**, 445 (1975).

[15]Yogesh K. Vohra, Hui Xia, Huan Luo, and Arthur L. Ruoff, Appl. Phys. Lett. **57**, 1007 (1990).

[16]Arthur L. Ruoff, Hui Xia, Huan Luo, and Yogesh K. Vohra, Rev. Sci. Instrum. **61**, 3830 (1990).