New High-Pressure Phase Transition in Zirconium Metal

Hui Xia, Steven J. Duclos, Arthur L. Ruoff, and Yogesh K. Vohra
Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853

(Received 19 October 1989; revised manuscript received 22 November 1989)

Phase transitions in the group-IV transition metal zirconium were studied by the energy-dispersive x-ray-diffraction technique with a synchrotron source to a pressure of 32 GPa. A first-order phase transition between an ω phase and a bcc phase (isostructural with group-V transition elements) was observed during compression and decompression in a pressure range of 30 ± 2 GPa, which is in qualitative agreement with the recent first-principles theoretical predictions. The observation of the bcc phase in Zr (a group-IV element) under pressure at room temperature signifies a pressure-induced electronic configuration similar to that of a group-V element.

PACS numbers: 64.70.Kb, 61.10.−i, 62.50.+p, 64.30.+t

Crystal structures of elemental metals tend to have certain sequences when viewed as functions of atomic number or hydrostatic pressure. The most prominent example of this phenomenon is the d transition metals, where all three transition series, excluding the four magnetic $3d$ metals, show the canonical hcp→bcc→hcp→fcc sequence as their atomic numbers increase, or as their d bands become progressively filled.[1-4] It is believed that the d electrons play a critical role in determining the crystal structures of these transition metals. Similar transition-metal structure sequences are 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.[1,2] This pressure-induced phase-transformation sequence has received extensive experimental as well as theoretical attention. Calculations of the crystal structures using one-electron theory, based on electron transfer from the s to the d band under compression, are given in reviews by McMahan[3] and Skriver.[4]

The phenomenon of electron transfer from the s to the d band under pressure is well known for transition metals.[5] Physically, this phenomenon can be attributed to the greater fraction of the atomic volume occupied by the sp core in transition metals. The bottom of the s band (B_s) rises faster than that of the d band (B_d) because the s-band electrons have a greater increase in kinetic energy than the d electrons since they are repelled by the orthogonality effect as they are more confined to the core region under compression. This larger increase in B_s reduces the spacing between the s and d bands, and causes the increase in occupancy of the d band. It is this increase in d-band occupancy with pressure of the transition metals with a partially filled d band like Ti, Zr, and Hf that makes the pressure effects equivalent to alloying with d-rich metals. Some model calculations[6,7] show that the pressure-induced electron transfer from the s band to the d band is greater for the first several columns of transition element series. Therefore, the transition metals in the first several columns are expected to show phase transitions at modest pressures, while ultrahigh pressures greater than 200 GPa will likely be required for the phase transitions of the metals near the middle of the transition element series.[2]

In this paper we present the first experimental evidence for the pressure-induced structural phase transformation of a group-IV transition metal to the body-centered-cubic structure of group-V transition metals. The sample we used in this experiment is the group-IV transition metal zirconium, which crystallizes in a hcp structure (α phase) at ambient conditions, and is known to transform to a bcc structure (β phase) above 1135 K at atmospheric pressure. The Zr metal was first studied by Bridgman,[8] who found a resistance discontinuity at 5.9 GPa indicative of a first-order phase transition. Subsequent x-ray-diffraction experiments by Jamieson[9] indicated this transformation to be from hcp to a hexagonal structure (ω phase, three atoms per unit cell). Jayaraman, Klement, and Kennedy[10] measured the slope of various phase boundaries at high temperatures and high pressure and located the triple point in the phase diagram of Zr. The α-ω phase transformation in Zr has hysteresis associated with it and the equilibrium transformation pressure is now believed to be 2.2 GPa.[1,11,12] The room-temperature x-ray-diffraction data of the Zr sample presented here show a new structural phase transition in a pressure range of 30 ± 2 GPa from the ω phase to a β phase (the structure of group-V transition metal niobium). This result is in qualitative agreement with the theoretical estimation of Gyanchandani *et al.*,[13] based on the linear-muffin-tin-orbital (LMTO) method, though the theoretical transition pressure of 15 GPa is lower than the experimental value.

The energy-dispersive x-ray-diffraction (EDXD) data were collected at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory and at the Cornell High Energy Synchrotron Source (CHESS). Details of the experimental apparatus and techniques can be found in Refs. 14 and 15. We used a high-pressure cell with diamond-anvil tips 640 μm in diameter. Several pieces of Zr foil 25 μm thick with a purity of 99.996% were placed in a sample region 150 μm in diameter. Two different experiments were done on Zr metal. The first one employed gold as an internal pressure marker while the second experiment was done with only Zr in the sample hole along with a pressure-transmitting medium (4:1 ethanol:methanol) to avoid the interference due to the marker material. The sample pressure in the first experiment was determined by the x-ray diffraction of gold power spread over the sample region, and the isothermal equation of state of gold is given by Jamieson, Fritz, and Manghnani.[16] In the second experiment pressures were estimated from the measured equation of state of Zr from the first experiment.

The Zr sample was preloaded to a pressure of about 7 GPa and x-ray-diffraction data at this pressure showed that the sample was in the ω phase, which is in agreement with previous high-pressure studies.[8-12] It is known that a body-centered-cubic structure (β phase) is obtained by the splitting of the alternating (001) plane along the c axis of a ω structure into two (111) planes of the β phase. Therefore, the x-ray-diffraction spectrum of the ω phase contains all the diffraction lines of the β phase and some additional diffraction lines resulting from its superlattice structure. The energy-dispersive x-ray-diffraction spectra of Zr during the compression and decompression cycles are shown in Fig. 1. The diffraction patterns are excellent and fourteen diffraction peaks were observed in the ω phase [Fig. 1(a)] at 31.1 GPa before the transformation. On further compression, seven diffraction peaks disappeared abruptly and a pure bcc phase was formed at 31.6 GPa [Fig. 1(b)]. On decompression, the seven superlattice reflections reappeared abruptly and a back transformation was completed at 31.0 GPa [Fig. 1(c)]. Although this second experiment shows a sharp transformation at 31 GPa, in our first experiment with the pressure marker Au and under nonhydrostatic pressure conditions with no pressure medium, the transformation onset was seen at a pressure of 28 GPa. Combining all the experimental uncertainties and hysteresis we give the equilibrium transformation pressure as 30 ± 2 GPa. This is an unusually clear illustration of a transformation from a low-symmetry crystal structure to a high-symmetry parent structure at high pressure. The Zr sample remains in the bcc (β) structure to at least 32 GPa, the upper pressure limit of the experiments.

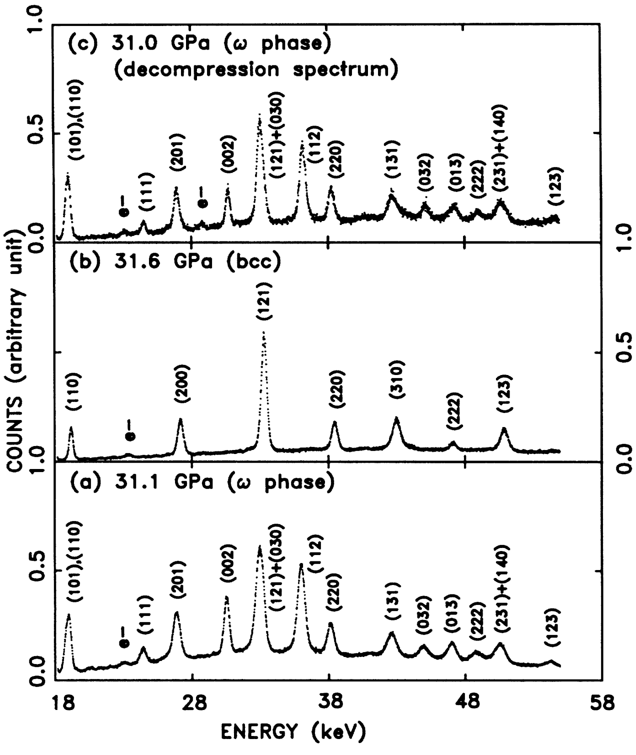

FIG. 1. Energy-dispersive x-ray-diffraction spectra of the Zr sample at various pressures and room temperature. (a) ω phase during compression at 31.1 GPa ($Ed = 44.242 \pm 0.009$ keV Å). (b) bcc phase during compression at 31.6 GPa ($Ed = 44.448 \pm 0.006$ keV Å). (c) Reversal of transformation during decompression ($Ed = 44.425 \pm 0.006$ keV Å). The symbols e^- are escape peaks of the Ge detector. The spectra were collected at the B1 station at CHESS and the typical data collection time for each spectrum is 15 min.

The c/a ratio of Zr in different phases is shown in Fig. 2. The c/a ratio for the ω phase of Zr is 0.625 ± 0.002, and was found to be pressure independent within the experimental errors. It is interesting to point out that this value is slightly higher than the ideal c/a ratio 0.612 of the ω phase.

From the x-ray-diffraction spectra, the reduced volume V/V_0 of Zr versus pressure was calculated, and is shown in Fig. 3. The low-pressure data of the α and ω phases up to about 10 GPa are from results of Olinger and Jamieson.[11] The data were fitted by a Birch first-order equation of state[17]

$$P = \tfrac{3}{2} B_0 (x^{7/3} - x^{5/3}) [1 + \tfrac{3}{4} (B_0' - 4)(x^{2/3} - 1)] , \quad (1)$$

where $x = V_N/V$, V is the volume per Zr atom, V_N is a

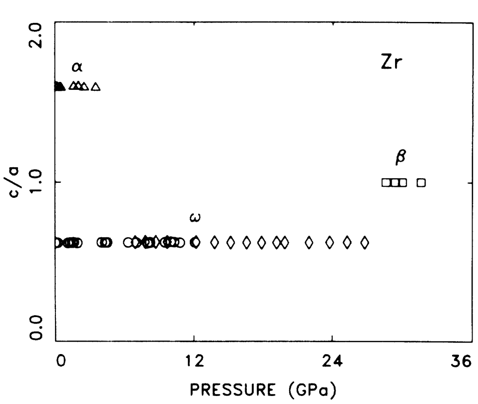

FIG. 2. The measured axial ratio of Zr for α (hcp), ω (ω hexagonal), and β (bcc) phases. ◇ and □ are from our present experiment; △ and ○ are from Ref. 11.

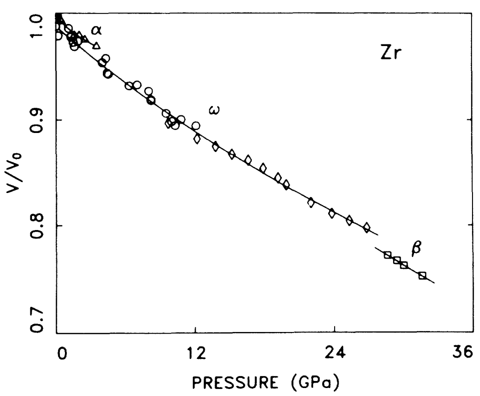

FIG. 3. The measured equation of state of Zr for the three phases α (hcp), ω (ω hexagonal), and β (bcc). The solid curves are the fit of the Birch first-order equation of state to the data (see text for details). ◇ and □ are from our present experiment; △ and ○ are from Ref. 11.

fitting parameter which corresponds to the extrapolated volume per atom of the phase under consideration at zero pressure, B_0 is the isothermal bulk modulus at zero pressure, and B_0' is the pressure derivative of the isothermal bulk modulus evaluated at zero pressure.

The fits to the various phases of Zr to the Birch first-order equation are shown by solid curves in Fig. 3. We fixed V_N for the ω phase from the results of the previous experiment,[11] $V_N/V_0=0.987$. The calculated coefficients of the Birch first-order equation for the ω phase are $B_0=104$ GPa, and $B_0'=2.05$. We estimate a volume decrease of about 1.6% at the ω-to-β phase transformation from the extrapolation of the Birch first-order equations of state of both structures to the transition pressure of 30 GPa.

According to the compilation of equilibrium phase diagrams[18] of the group-IV transition metals, the β phase is a high-temperature phase with positive slope dT/dP of the boundary of the ω to β phase (6 °C/GPa as measured by Jayaraman, Klement, and Kennedy[10]). The discovery of the transformation from the ω to β phase at room temperature and high pressure indicates that the high-temperature phase can also be obtained purely by an application of pressure, which has important implications for the phase diagram of Zr. There are two distinct possibilities for the phase diagram. One of them is that the high-pressure and high-temperature stability fields of the bcc (β) phase are connected, which implies a negative slope dT/dP of the ω-β phase boundary at room temperature and high pressure. The other possibility is that the two stability fields of the β phase are two distinct regions separated by the ω phase, which would mean that there is another triple point at high pressure and high temperature. High-pressure, high-temperature x-ray-diffraction studies are needed to establish the complete phase diagram. It is well known that a large number of metallic elements transform to the bcc structure at high temperature at atmospheric pressure before melting. This is believed to be due to the more open structure (higher vibrational entropy) associated with the bcc phase.[19] However, the formation of the bcc phase in the group-IV transition metal Zr during cold compression is purely an electronic effect and signifies a pressure-induced electronic configuration similar to that of group-V elements.

This discovery of the bcc phase of Zr under pressure gives the first experimental evidence of a pressure-induced structure sequence in transition metals and, from a crystal-structure point of view, the first experimental evidence of a phase transformation from a group-IV transition metal to a group-V transition metal. Furthermore, it confirms the one-electron theory about the crystal structures of transition metals based on the idea of electron transfer from the s band to the d band under compression. We also suggest that the phase transition seen in shock waves[20] in Zr at 26 GPa and 540 K may be due to the ω-to-β phase transition (assuming a negative slope of the ω-β phase boundary) as the pressure is close to our result of 30 ± 2 GPa. We expect a similar pressure-induced transformation in the other group-IV transition metals Ti and Hf. We also expect that, with the current multimegabar pressure capability of diamond-anvil cells, pressure-induced structure sequences can be experimentally studied for the transition metals near the middle of the transition element series.

We thank C. A. Vanderborgh and Dr. D. E. Cox for their help. We thank Dr. J. W. Shaner of Los Alamos National Laboratory for many useful discussions. We acknowledge support of the Division of Materials Research, National Science Foundation Grant No. DMR 86-12289. We also acknowledge the use of the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy Grant No. DE-AC02-76CH0016 and Cornell High Energy Synchrotron Source (CHESS). One of us (S.J.D.) thanks AT&T for support.

---

[1] Y. K. Vohra, J. Nucl. Mater. **75**, 288 (1978).

[2] R. S. Hixson, D. A. Boness, J. W. Shaner, and J. A. Moriorty, Phys. Rev. Lett. **62**, 637 (1989).

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

[4] H. L. Skriver, Phys. Rev. B **31**, 1909 (1985).

[5] D. G. Pettifor, J. Phys. F **4**, 613 (1977).

[6] Y. K. Vohra, Acta Metall. **27**, 1671 (1979).

[7] I. V. Svechkarev and A. S. Paniflov, Phys. Status Solidi (b) **63**, 11 (1974).

[8] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **81**, 165 (1952).

[9] J. C. Jamieson, Science **140**, 72 (1963).

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

[11] B. Olinger and J. C. Jamieson, High Temp.-High Pressure **5**, 123 (1973).

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

[13] J. S. Gyanchandani, S. C. Gupta, S. K. Sikka, and R. Chidambaram, in Proceedings of the International Conference on High Pressure Science and Technology, Paderborn, West Germany, July 1989 (to be published).

[14] K. E. Brister, Y. K. Vohra, and A. L. Ruoff, Rev. Sci Instrum. **57**, 2560 (1986).

[15] M. Baublitz, Jr., V. Arnold, and A. L. Ruoff, Rev. Sci. Instrum. **52**, 1616 (1981).

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

[17] F. Birch, J. Geophys. Res. **83**, 1257 (1978).

[18] A. R. Kutsar, Fiz. Metal. Metalloved **40**, 786 (1975).

[19] C. Zener, Phys. Rev. **71**, 846 (1947).

[20] 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. 293.