Crystal structures of group IVa metals at ultrahigh pressures

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High-pressure energy-dispersive x-ray-diffraction studies were carried out on the group IVa metals hafnium (Hf) to 252 GPa (to a volume compression V/V_0 of 0.48) and titanium (Ti) to 87 GPa using a synchrotron source. Two new structural phase transformations between an hcp phase and an ω phase and between the ω phase and a bcc phase (isostructural with group V transition metals) were observed during both compression and decompression in Hf. Equilibrium transformation pressures for Hf are 38 ± 8 and 71 ± 1 GPa for the hcp-to-ω and ω-to-bcc phase transformations, respectively, at room temperature. In Ti, only the hcp-to-ω phase transition was observed above 8 GPa, and the ω phase was stable to 87 GPa. The crystal structure sequences of Ti, Zr, and Hf at ultrahigh pressures are discussed.

Transition metals in the first several columns of the Periodic Table, such as titanium (Ti), zirconium (Zr), and hafnium (Hf), and near the middle of the transition-element series, such as chromium (Cr), molybdenum (Mo), and tungsten (W), are expected to have a structural phase transition sequence under ultra high-pressure conditions which is similar to the canonical hcp→bcc →hcp→fcc structural sequence of nonmagnetic transition metals as their atomic numbers increase. It is believed that this structural transition sequence is due to electron transfer from an s band to a d band under compression.[1-3]

Recently we reported that Zr, a group IV transition metal, shows a phase transition from an ω phase to a bcc phase (isostructural with group V transition elements) at a pressure of 30 ± 2 GPa.[4] It is known that Hf, like the other group IV transition metals Ti and Zr, transforms from an hcp (α phase) into a bcc (β phase) structure at high temperature. However, the transformation temperature of Hf is 2030 K, about a factor of 2 higher than that of Ti (1155 K) or Zr (1135 K).[5] Bridgman[6] and Jayaraman[7] did resistivity measurements under pressure to about 10 GPa on group IVa metals and found that the resistance jumps in Ti and Zr are indicative of phase transformations from α to hexagonal ω phases.[8] These early measurements indicated no phase transition in Hf to 10 GPa. It is also known that Zr-Hf alloys show hcp-to-ω phase transformations under high pressure and that the transition pressure increases linearly with Hf content.[9] From the alloy data, the hcp-to-ω phase transformation in pure Hf was predicted to be 60 GPa.[9] This transformation has not yet been reported under static pressure. There is also no theoretical calculation for the structural phase transition pressures in pure Hf. McQueen *et al.*[10] measured Hugoniot PV data for Hf and found only one discontinuity at 40 GPa and 725 K in the shock velocity (U_s) versus particle velocity (U_p) plot indicative of a phase transition in Hf. Subsequent shock-wave studies by Bakanova *et al.*[11] show that there are two discontinuities, one at 45 GPa (863 K) and another at 60 GPa (1393 K) indicative of two phase transitions in Hf. We undertook systematic structural investigations of Hf and Ti to ultrahigh pressures to understand the structural systematics of phase transformations in group IV transition metals.

In this experiment we discovered two new structural phase transitions in Hf under high pressures to 252 GPa. The equilibrium phase transformation pressure was found to be 38 ± 8 GPa for the transition from the ambient hcp phase to an ω phase and 71 ± 1 GPa for the transition from the ω to the bcc phase (a group V transition-metal structure). Both of the transition pressures in Hf are higher than for Zr.[4,12] Hf is stable in the bcc phase over a wide range of pressures of 71–252 GPa (to a volume compression of 0.48), the highest pressure achieved in this experiment. The back transformations of the Hf sample from the bcc to the ω phase and from the ω phase to the hcp phase were also observed during decompression. Therefore, the ω phase of Hf metal is not metastable, which is different from that observed in Zr. The ω phase of Ti was found to be stable to 87 GPa and no transformation to the bcc was observed.

The energy-dispersive x-ray-diffraction (EDXD) data were collected at the B1 station at the Cornell High Energy Synchrotron Source (CHESS). Details of the experimental apparatus and techniques can be found in Ref. 13. Three separate experiments were done with different diamond anvils. In the first experiment we used a pair of double-beveled diamond anvils with a center flat size of 50 μm in diameter with the first bevel angle of 7° to 175 μm and an additional second bevel angle of 3° to 300 μm in culet diameter. Similarly designed diamond anvils used in our earlier experiment with rhenium gasket generated pressures to 245 GPa.[14] Hf powder sample with a purity of 99.6% (with a trace impurity of Zr) mixed with Pt powder (25 wt %) was placed in a sample region of about 50 μm in diameter. X-ray-diffraction studies were done with this high-pressure cell to 252 GPa. In the second experiment we used a pair of flat diamond anvils with a culet size of 200 μm in diameter. The Hf and Pt

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mixtures were placed in a sample region of about 75 μm in diameter. The sample pressure in this cell was increased to 81 GPa and the sample was then decompressed to study the reverse transformations. Both of the experiments employed platinum as an internal pressure marker. The isothermal equation of the state of platinum as derived from shock-wave data is given by Holmes *et al.*[15] The Ti sample was studied to 87 GPa using ruby as a pressure marker in the third experiment.

From the energy-dispersive x-ray-diffraction data, we found that the Hf sample remained in the hcp phase up to 45.8 GPa ($V/V_0=0.778$) and then started to transform into the ω-hexagonal structure. The transformation was completed at 58.3 GPa ($V/V_0=0.724$). This result is in agreement with the shock-wave result.[10] Upon further increasing the pressure, Hf was found to start to transform into a bcc structure at 71.5 GPa ($V/V_0=0.691$) with the transformation completed at 78.4 GPa ($V/V_0=0.664$). The sample remained in the bcc phase over a wide pressure range and excellent diffraction data was obtained to 252 GPa ($V/V_0=0.483$), the upper pressure limit of this experiment. Figure 1(a) shows EDXD patterns with nine diffraction peaks in the hcp phase at 12.6 GPa. Eight peaks in the ω phase at 65.8 GPa are shown in Fig. 1(b) and four peaks in the bcc phase at 252 GPa are shown in Fig. 1(c). The Pt pressure marker peaks are also present in all the diffraction spectra in Fig. 1. X-ray-diffraction measurements during decompression were also made in the second experiment. The start of the back transformations from the bcc phase to the ω phase and the ω phase to the hcp phase were observed during the decompression. The sample finally transformed completely back to the hcp phase at 19.3 GPa during decompression. Fluorescence lines from the trace impurity Zr contained in the Hf sample were observed in the low-energy range which is not shown in Fig. 1; however, no diffraction peaks from Zr impurity were observed. A complete list of the starting and ending transformation pressures for all the forward and backward phase transitions between the hcp phase, ω phase, and bcc phase for Hf is displayed in Table I. The equilibrium transformation pressures shown in the table are calculated from the average of the starting transformation pressures of corresponding forward and backward phase transitions. Figure 2 shows a representative EDXD spectrum of the ω phase of Ti at 49.4 GPa. The superlattice reflections of the ω phase persist to the highest pressure of 87 GPa ($V/V_0=0.65$) indicating no phase transformation to the bcc phase.

From the V/V_0 data we found that there is a small volume change during the phase transformation from the hcp to the ω phase as well as during the phase transformation from the ω phase to the bcc phase. Therefore, both of the phase transformations observed in Hf are first-order phase transitions. The volume decreases during the transformations $(V_I-V_{II})/(V_I)$ (where V_I and V_{II} are volume per atom before and after the phase transformation of Hf) are estimated to be about 0.54% at 38 GPa for the transition from the hcp to the ω phase and 2.1% for the transition from the ω to the bcc phase at 71 GPa.

It is known that the bcc structure of Hf is a high-temperature phase.[5] The discovery of the room-temperature ω-to-bcc phase transformation under high pressure indicates that the high-temperature bcc phase can also be obtained purely by an application of pressure in Hf. We also suggest that the high-temperature phase transitions seen in shock waves[10] in Hf at 45 GPa (590 °C)

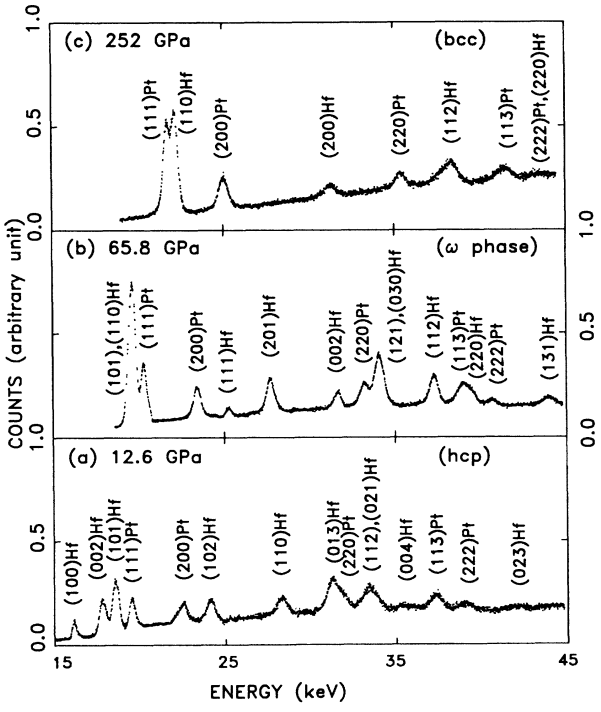

FIG. 1. Energy-dispersive x-ray-diffraction spectra of Hf at various pressures and room temperature. (a) hcp phase at 12.6 GPa. ($Ed=43.658\pm0.007$ keV Å.) (b) ω phase at 65.8 GPa. ($Ed=43.658\pm0.007$ keV Å.) (c) bcc phase at 252 GPa. ($Ed=43.645\pm0.006$ keV Å.) The spectra were collected at the B1 station at CHESS and the typical data collection time for each spectrum is 30 min.

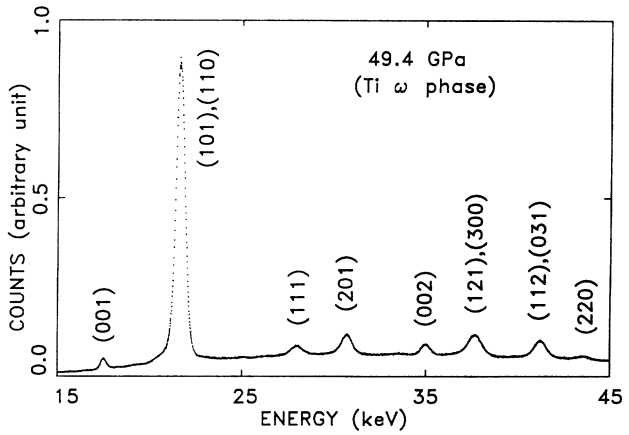

FIG. 2. Energy-dispersive x-ray-diffraction spectra of the ω phase Ti at 49.4 GPa and room temperature. ($Ed=45.664\pm0.003$ keV Å.) The spectra were collected at the B1 station at CHESS and the collection time for the spectrum is 45 min.

TABLE I. Summary of the transition pressures between the α-ω and ω-β phases of Hf measured during compression and decompression. The equilibrium transformation pressures between the phases are calculated to be the averages of the corresponding forward and backward transition pressures.

Transition pressures of Hf metal (GPa)		
	Start	Complete
α-to-ω	45.8	58.3
ω-to-α	30.0	19.3
P_0 equilibrium	38±8	
ω-to-β	71.5	78.4
β-to-ω	<71.5	65.8
P_0 equilibrium	~71±1	

and 60 GPa (1120 °C) may be due to the α-to-ω and the ω-to-bcc phase transitions as the pressures are close to our room-temperature static-pressure results of 38 GPa ($V/V_0=0.798$) and 71 GPa ($V/V_0=0.693$), respectively. These static transition pressures and volumes should be compared with the corresponding transformations in Zr at 2.2 GPa ($V/V_0=0.977$) and 30 GPa ($V/V_0=0.764$), respectively. It is also interesting to point out that, similar to our previous Zr data,[4] the transformation pressure of Hf from the ω-to-bcc phase measured in these room-temperature experiments (71±8 GPa) is higher than that obtained from the shock-wave result[10] obtained at high temperature, which implies a negative slope (dT/dP) for the β-ω phase boundary at room temperature.

It is interesting to point out that the $\alpha \rightarrow \omega \rightarrow \beta$ structure sequence is now confirmed in Zr and Hf and the ω-β transition in Ti if any is higher than 87 GPa. The α-ω transformation pressure in Hf is more than an order of magnitude higher than Ti and Zr. The α phase had been compressed by 20% in Hf as compared to only 2.3% in Zr at the α-ω phase transformation. This difference in volume compression at the first phase transformation is significant. On the other hand, the ω-β transformation pressure appears to be higher in Ti as compared to Zr and Hf. These experimental facts cannot be explained by a simple model of d-band occupancy and s-d transfer effects. The shape of the Fermi surface in group IVa metals at high pressure may also play a role in the phase transitions. Additional information on the changes in band structure with the pressures of Ti, Zr, and Hf are necessary to interpret the experimental results.

In this experiment, Hf showed a wide range stability in the bcc structure from 71 to at least 252 GPa. This result can be explained by the high stability field of the bcc phase in group V and group VI transition metals. From the decompression x-ray-diffraction data obtained in this experiment, we found that the phase transformation of Hf between the α and ω phases is sluggish with a large hysteresis while the phase transformation between the ω and bcc phases is sharp. This phenomenon is similar to the results for Zr.[4] In addition, we also found that Hf finally transformed back to the hcp structure completely from the ω phase during decompression at a pressure of 19.3 GPa. This result indicates that the ω phase is not metastable for Hf, which is different from the results of Ti and Zr. The ω-to-bcc phase transformation in Ti is higher than 87 GPa. First-principle theoretical calculations are needed to explain the observed systematics of phase transformation in group IV transition metals. In particular, the question of the quantitative s-d transfer rate under high pressure should be computed for Ti, Zr, and Hf metals.

Note added in proof. Recent theoretical calculations on structural stability of Hf under pressure are in agreement with our experiment.[16]

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