Novel γ-Phase of Titanium Metal at Megabar Pressures

Yogesh K. Vohra and Philemon T. Spencer
Department of Physics, University of Alabama at Birmingham (UAB), Birmingham, Alabama 35294-1170

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Group IV transition metals titanium, zirconium, and hafnium are expected to transform from an ambient hexagonal close packed (hcp, α-phase) to a body centered cubic (bcc, β-phase) at high pressures. This transition path is usually facilitated by the occurrence of an intermediate hexagonal phase (distorted bcc, ω-phase). The existence of a bcc phase in zirconium and hafnium at high pressures has been known for the past ten years; however, its occurrence in titanium has been theoretically predicted but never observed. We report a novel unexpected transformation in titanium metal from an omega phase to an orthorhombic phase (distorted hcp, γ-phase) at a pressure of 116 ± 4 GPa.

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The phase transformations in titanium, zirconium, and hafnium metals at high pressures and high temperatures were first reported in x-ray diffraction studies by Jamieson [1] and in differential thermal analysis by Jayaraman and co-workers [2]. Group IV transition metals titanium, zirconium, hafnium, and their alloys have tremendous scientific and technological interest. The fundamental interest in these materials in the transition metal series stems from the fact that they have a narrow d-band in the midst of a broad sp-band, which has an impact on their electronic and superconducting properties. The electronic transfer between the broad sp-band and the narrow d-band is the driving force behind many structural and electronic transitions in these materials [3–5]. The industrial demand of these materials is in aerospace, medical, and nuclear fields where their high strength, light weight, corrosion resistance, and the nuclear absorption cross sections are of prime interest. The mechanical properties of these metals and alloys can be greatly improved by controlling the crystallographic phases present and optimizing the microstructure of the material. Pressure is a very important variable in causing phase transformations in these elements [5–7], and some of the pressure induced phases can be retained in a metastable form after removal of pressure.

Titanium crystallizes in a hexagonal close packed structure at ambient conditions but transforms to a body centered cubic phase at high temperatures above 1155 K [6]. The group IV transition metal series shows the following crystallographic sequence with an increasing number of d-electrons caused by alloying with d-electron rich neighbors such as V, Nb, and Ta or by increasing pressure [8].

$$\begin{aligned}&\text{hexagonal close packed (hcp, }\alpha)\\&\quad\rightarrow \text{omega phase } (\omega)\\&\quad\rightarrow \text{body centered cubic (bcc, }\beta)\,.\end{aligned}$$

The increase in the number of d-electrons with pressure is caused by the lowering of the d-band relative to the s-band with increasing pressure or reducing volume. This can be conceptually thought to be due to the fact that s-electrons are more extended in space and, when squeezed, see the repulsive effects of the neighboring electrons more than the relatively compact and localized d-electrons. This gives rise to a relative increase in the energy of sp-electrons as compared to d-electrons with increasing pressure. Hence, with increasing pressure, one expects to see $s \rightarrow d$ electron transfer and, hence, eventual transformation to the bcc phase in these metals. Based on these simple arguments and backed by first principles theoretical calculations, one would expect titanium, zirconium, and hafnium metals to adapt bcc phase at high pressures. These expectations were realized in zirconium where a bcc phase was observed above 35 GPa [9,10] and in hafnium where a bcc phase was observed above 71 GPa [11] at room temperature. First principles calculations [7] on titanium predict an omega phase to the bcc phase transformation at a pressure of 58 GPa and a calculated volume compression $V/V_0 = 0.66$. However, earlier high-pressure studies on titanium indicated that the omega phase was stable to the highest pressure of 87 GPa (volume compression $V/V_0 = 0.65$) reached in this study [11], and transformation to the bcc phase was not observed. It should be added that the ultrahigh-pressure x-ray diffraction studies on titanium are made difficult by its low x-ray scattering cross section as compared to zirconium and hafnium. Typical samples of 25 μm in diameter and 5–10 μm in thickness are employed at ultrahigh pressures in a diamond anvil cell. Several megabar pressure experiments have been carried out on titanium in the past few years; however, it has been difficult to observe more than 1–2 strong diffraction peaks at megabar pressures (100 GPa), thus making structural studies at high pressures extremely challenging. In this report, we have carried out energy dispersive x-ray diffraction studies on titanium samples of 25 μm in diameter using a focused x-ray beam of 10 μm by 10 μm. These studies were carried out at the X-17C beam line at the National Synchrotron Light Source (NSLS). The Kirkpatrick-Baez focusing mirrors [12] produce a beam that is 10–20 times

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more intense than the conventional 10 μm × 10 μm collimated beams and is ideal for studying low atomic number materials at pressures above a megabar (100 GPa).

Titanium was studied in a diamond anvil cell to 146 GPa at room temperature employing diamonds of 65-μm central flat, 7.5° bevel, and a culet size of 350 μm in diameter. A sample hole of 25 μm in diameter was filled with titanium foil (99.8% purity) along with a copper pressure standard (99% purity). The room temperature equation of state of copper obtained from the shock compression data was used in calibration of pressure, once the volume of the copper pressure standard was measured by x-ray diffraction [13]. In addition, a separate high-pressure experiment to 25 GPa was performed to provide accurate pressure-volume data points in the low-pressure range. This low-pressure experiment to 25 GPa was conducted with a 600-μm flat diamond and with a sample size of 150 μm in diameter.

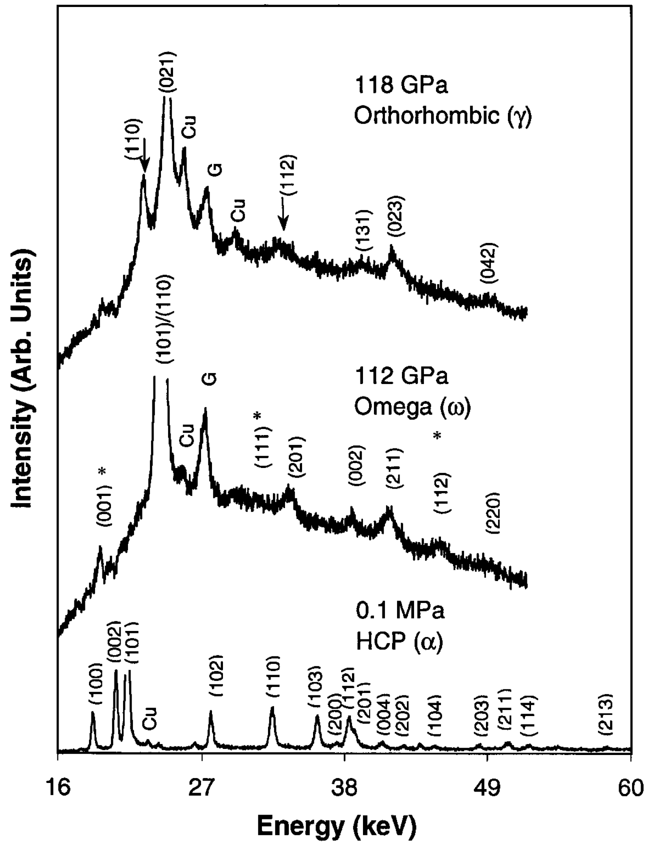

FIG. 1. Energy dispersive x-ray diffraction spectrum of titanium sample and copper pressure standard at various pressures in a diamond anvil cell taken with a microfocused 10 μm × 10 μm synchrotron x-ray beam. The diffraction angle 2θ is 15° ($Ed = 47.5$ keV Å). The characteristic (001), (111), and (112) reflections of the omega phase marked by "asterisks" disappear at the phase transition at 116 GPa, and new peaks marked by "arrows" appear at the transition to the orthorhombic phase. The spectrums have been scaled to show weak diffraction peaks, and peak marked G is from gasket material, while peaks marked Cu are from copper pressure marker. The peaks labeled with miller indices (hkl) are from titanium sample.

Figure 1 shows the energy dispersive x-ray diffraction spectrum of the titanium sample and the copper pressure marker at various pressures in a diamond anvil cell recorded at a diffraction angle $2\theta = 15°$. The ambient pressure hcp phase of titanium has lattice parameters $a = 2.957 \pm 0.006$ Å and $c = 4.685 \pm 0.009$ Å, with c/a ratio $= 1.585$ (volume/atom, $V_0 = 17.735$ Å^3/atom). On increasing pressure, the hcp to omega phase transition is observed at 9 GPa with a volume decrease $\Delta V/V = -1.9\%$. The omega phase in titanium is found to be stable up to pressure as high as 112 GPa. The stability of the omega phase is confirmed by the existence of a characteristic (001) basal plane reflection clearly visible at 112 GPa in Fig. 1. The measured lattice parameters for the omega phase at 112 GPa are $a = 3.876 \pm 0.009$ Å and $c = 2.473 \pm 0.006$ Å with c/a ratio $= 0.638$. At 116 ± 4 GPa, we observe a novel transformation where characteristic peaks (001), (111), and (112) of the omega phase, indicated by asterisks in Fig. 1, disappear and new peaks, indicated by arrows, appear. These new peaks correspond to (110) and (112) diffraction peaks of the orthorhombic γ-phase. These changes in the diffraction pattern are reversible on decreasing pressure, confirming a reversible phase transformation at 116 GPa. The observed diffraction pattern at 118 GPa (Fig. 1) has been indexed to an orthorhombic phase with $a = 2.388 \pm 0.005$ Å, $b = 4.484 \pm 0.009$ Å, and $c = 3.915 \pm 0.008$ Å. The choice of four atoms/cell gives a volume of 10.48 Å^3/atom or volume compression V/V_0 of 0.591. The measured volume decrease on transformation from the omega phase to the orthorhombic phase at 120 GPa is $\Delta V/V = -1.6\%$. This orthorhombic phase was found to be stable to the highest pressure of

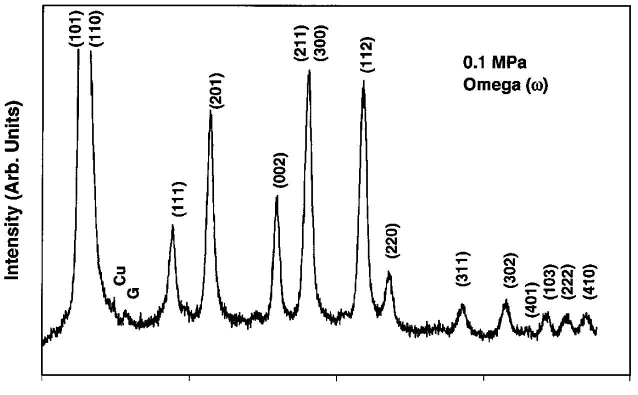

FIG. 2. Energy dispersive x-ray diffraction of the titanium sample after release of pressure showing retention of the omega phase in a metastable condition. The diffraction angle 2θ is 15° ($Ed = 47.5$ keV Å). The small peak marked G is from gasket material while peaks marked Cu are from copper pressure marker.

TABLE I. Crystallographic data, pressure range of stability, and equation of state parameters for the three known phase of titanium under high pressure. The β parameter in the modified universal equation of state was set to zero for the three phases.

Phase of titanium	Pressure range of existence	Zero pressure volume $Å^3$/atom	Bulk modulus at zero pressure B_0 (GPa)	Equation of state parameter η
Hexagonal close packed, α-phase	0–9 GPa	17.735	102	12.1
Hexagonal ω-phase	0–116 GPa	17.37	142	1.92
Orthorhombic γ-phase	116–146 GPa	17.05	152	1.44

146 GPa or to a volume compression $V/V_0 = 0.545$. On decreasing pressure from 146 GPa, the orthorhombic phase back-transformed to the omega phase at 112 GPa, with the reappearance of the characteristic (001) reflection of the omega phase. A complete release of pressure to ambient conditions in our 146 GPa experiment resulted in a phase mixture of hcp and omega phase. On the other hand, pressure release from 25 GPa to ambient conditions resulted in the retention of a pure omega phase as shown in Fig. 2. This difference in the unloading behavior in the two experiments is related to the difference in the shear stresses present in these experiments. It is well known that the presence of shear forces reduces the hysteresis associated with the hcp-omega transition in the group IV transition metals, and a shear induced back-transformation from omega to hcp phase is observed during decompression [14]. Therefore, higher shear stress present in our 146 GPa experiment results in a partial conversion of omega to hcp during decompression. The measured lattice parameters of the omega phase at ambient pressure are based on a fit to the 21 diffraction peaks and are $a = 4.598 \pm 0.009$ Å and $c = 2.822 \pm 0.006$ Å, with c/a ratio of 0.614 (Fig. 2).

The equation of state employed in this analysis was the modified universal equation of state (MUEOS) [15,16] as described below:

$$\ln H = \ln B_0 + \eta(1 - x) + \beta(1 - x)^2,$$

where $x^3 = V/V_0$ is the volume compression, $\eta = 1.5(B_0' - 1)$, and $H = Px^2/[3(1 - x)]$. V_0, B_0, and B_0' are the atomic volume, isothermal bulk modulus, and the first pressure derivative of the bulk modulus at ambient pressure. The shock data for copper [13] when fitted to the MUEOS gives $B_0 = 143.7$ GPa, $B_0' = 3.904$, and $\beta = 13.77$. These parameters were employed in our pressure calculations based on copper standard.

The pressure-volume curves for the three phases of titanium observed with increasing pressure were fitted separately to the MUEOS described above and the results are summarized in Table I. The equation of state data along with the MUEOS fits is shown in Fig. 3. The small volume discontinuities at 9 and 116 GPa in Fig. 3 correspond to an hcp to omega transition and omega to orthorhombic transition, respectively.

The orthorhombic (γ-phase) can be described as a distorted hcp structure. This orthorhombic distortion of an hcp structure results in cell parameters a, b, and c (Space Group Notation-*Cmcm*). The lattice parameters of the orthorhombic phase and the hcp phase are related: $a_{\text{ortho}} \cong a_{\text{hcp}}$, $b_{\text{ortho}} \cong \sqrt{3}\, a_{\text{hcp}}$, and $c_{\text{ortho}} \cong c_{\text{hcp}}$. The four atoms occupy $4c$ positions with coordinates $(0, y, \frac{1}{4})$, $(0, -y, \frac{3}{4})$, $(\frac{1}{2}, y + \frac{1}{2}, \frac{1}{2})$, and $(\frac{1}{2}, \frac{1}{2} - y, \frac{3}{4})$. The y-parameter can be determined from the experimentally measured intensity ratio of the (110) diffraction line relative to (021) and (002) in the orthorhombic phase. Table II shows the comparison between the observed and calculated d spacings and intensities for the diffraction data at 118 GPa. The experimental data at 118 GPa shown in Table II results in a y parameter of 0.10 (y parameter for hcp phase is 0.167). It should be added that the c/a ratio for the orthorhombic phase at 118 GPa is 1.639, which is close to the ideal value of 1.633 for the hcp phase. The b/a value is 1.878, which is considerably distorted from the ideal b/a value of 1.732 for the hcp structure. Therefore, our experiments indicate that most of the structural distortion of the hcp phase leading to γ-phase occurs in the ab plane of the orthorhombic lattice, as is evident from the b/a ratio and the displacement of atoms along the b axis (y parameter). The y

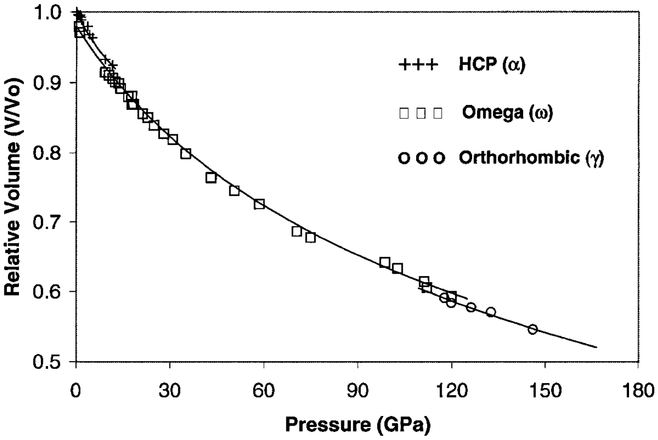

FIG. 3. The measured pressure-volume curve or equation of state of titanium to a pressure of 146 GPa at room temperature. All the experimental data points have been normalized to ambient pressure hcp volume of 17.735 $Å^3$/atom. The data for each of the three phases of titanium are plotted with a different symbol and the solid curve is a fit to the modified universal equation of state described in the text. The small volume changes or break in the curves are due to phase changes at 9 and 116 GPa.

TABLE II. The comparison between the observed and calculated interplanar spacings (d_{hkl}) and intensities for various diffraction peaks of titanium sample at a pressure of 118 GPa. The calculated values are based on an orthorhombic cell with $a = 2.388$ Å, $b = 4.484$ Å, and $c = 3.915$ Å with positional parameter $y = 0.10$. The asterisk (*) in a column means that the observed peak interfered with the copper pressure standard or buried in background.

(hkl)	d_{hkl} (Å) observed	d_{hkl} (Å) calculated	Intensity observed	Intensity calculated
(020)	*	2.242	*	4
(110)	2.108	2.108	46	50
(021)/(002)	1.946	1.945	100	100
(111)	*	1.856	*	46
(112)	1.431	1.434	19	45
(131)	1.202	1.205	17	32
(023)	1.130	1.128	27	12

parameter changes from $y = 0.167$ (hcp phase) to $y = 0.10$ (orthorhombic) phase.

The omega phase is an open structure with a packing fraction of 0.57, which is slightly larger than the value of 0.52 for the simple cubic phase, but is substantially lower than the packing fraction of 0.68 for the bcc structure and 0.74 for the hcp structure. Therefore, application of high pressure is expected to favor crystal structures with high packing fraction such as bcc or hcp structure. The theoretical calculations on titanium under high pressure find the bcc phase is to be lower in energy than the hcp or the omega phase at volumes less than 12 Å^3/atom [5,7]. This bcc phase stability is due to the specific spectral shape of the electronic density of states, which produces lower electronic states available in d-sublevels and, hence, favors the bcc structure. However, it is possible that the orthorhombic phase discovered in our experiments has d-sublevels, which are even lower in energy than the competing bcc and omega structures, and has an overall lowest electronic energy. Also, titanium is a model tetravalent system in which d-electron localization effects are dominant and f-electron effects are expected to be minimal. Thus, the high-pressure behavior of tetravalent titanium is important in understanding the behavior of more complex systems such as actinides under pressure where both d-electron localization effects and f-electron effects are important. This points to a clear need for more refined first principles theoretical calculations on tetravalent titanium to explain the occurrence of this novel orthorhombic γ-phase at megabar pressures and elucidate its differences with zirconium and hafnium under similar conditions.

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