

Titanium metal at high pressure: Synchrotron experiments and *ab initio* calculationsRajeev Ahuja,¹ Leonid Dubrovinsky,² Natalia Dubrovinskaia,² J. M. Osorio Guillen,¹ Maurizio Mattesini,¹ Börje Johansson,¹ and Tristan Le Bihan³¹*Condensed Matter Theory Group, Department of Physics, Uppsala University, Box 530, SE-751 21 Uppsala, Sweden*²*Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany*³*European Synchrotron Radiation Facility, F-38043 Grenoble, France*

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The high pressure behavior of titanium metal is investigated experimentally using angle dispersive synchrotron x-ray diffraction as well as theoretically using *ab initio* electronic structure methods. Our calculations predict a direct ω to bcc transformation around 80 GPa without any intermediate crystal phases. The β' (bcc-structure) Ti phase was experimentally observed to coexist with the ω phase at pressures between 40 and 80 GPa on compression at ambient temperature. High-temperature treatment at 80 GPa results in a formation of a new η phase with a monoclinically distorted bcc structure. On decompression the η phase transforms to the pure β' phase.

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The titanium group of elements and their alloys are very important materials both from technological and scientific point of view. Technologically, these materials have applications in the aerospace industry due to their light weight, static strength and stiffness and they do not degrade rapidly when the temperature is increased and they also show oxidation resistance. From the fundamental aspect, these elements are situated in the beginning of the transition metals series and their electronic structure is dominated by a comparatively narrow *d*-band hybridizing with a broad *s* band. Under pressure there is a transfer of *s* electrons into the *d* band. This rearrangement governs both the electronic and structural properties. Conventional ideas about the crystal structures of transition metals state that the most important parameter controlling the stability of a given structure is the *d*-occupation number. This is related to fact that the *d* density of states for different structure show characteristic element independent shapes.

The titanium group of elements are all stable in the hcp (α) structure under ambient conditions, but at high temperature they transform to the bcc (β) structure. It is now also well established experimentally that under pressure two of the elements of the titanium group (Zr and Hf) transform to the bcc phase even at ambient temperature and high pressure. In addition all three elements (Ti, Zr, and Hf) show a phase transition from the hcp to the ω phase under pressure.¹⁻³ On further compression, the ω phase transforms to the bcc phase in the case of Zr and Hf.³ The search for the missing high pressure bcc phase in titanium is still going on. Very recently, two groups have independently reported high pressure measurements for Ti in the megabar pressure range and Vohra and Spencer⁴ found a novel γ phase of Ti at megabar pressures. They showed that Ti transforms from the ω phase to an orthorhombic (γ) phase at 116.0 GPa. This phase remained stable up to the highest studied pressure of 146 GPa. Later, Akahama *et al.*⁵ have reported a new δ phase (distorted bcc) phase at 140 GPa beyond the intermediate γ phase. This δ phase was stable up to 220 GPa. Most surprisingly the two new studies did not show any sign of the expected bcc phase under high pressure. On the other hand, *ab initio* theoretical

calculations by Ahuja *et al.*⁶ have already predicted that the bcc phase in Ti should become stable under pressure already at a pressure below 100 GPa. However, in these calculations, the recently reported γ and δ phases were not taken in account. Recently, Joshi *et al.*⁷ have also performed theoretical high pressure study on Ti metal.

The main aim of the present work is to make another study of the high pressure behavior of Ti both experimentally (synchrotron x-ray diffraction) and theoretically (fully relaxed *ab initio* FPLMTO method). From these studies we will show that Ti under pressure indeed behaves in a similar way as its counterpart tetravalent metals, Zr and Hf.

The details of the electrically and laser-heated DAC experiments are described by Dubrovinsky *et al.*⁸⁻¹⁰ Powder x-ray diffraction data were obtained at ESRF (beam line ID30) with the Bruker CCD area detector using an x-ray beam of 0.3738 Å wavelengths and size of 10×12 μm. Detector-to-sample distance was varied from 170 to 220 mm. Diamonds were mounted on the seats made of cubic BN allowing us to collect the complete Debye rings to 0.9 Å. The collected images were integrated using the FIT2D program in order to obtain a conventional diffraction spectrum. The Rietveld refinements of powder x-ray diffraction data were carried out using the GSAS program.¹¹ As internal pressure standards and pressure medium we used NaCl powder mixed with the sample in the mass proportion approximately 1:4.

We have also performed calculations using the full potential linear muffin-tin orbital (FPLMTO) method¹² in which basis functions, electron densities, and potentials were calculated without any geometrical approximation. These quantities were expanded in spherical waves (with a cut-off $l_{\max}=8$) inside nonoverlapping spheres surrounding the atomic sites (muffin-tin spheres) and in a Fourier series in the interstitial region, between the spheres. We have used generalized gradient approximation (GGA) by Perdew, Burke, and Ernzerhof¹³ for the exchange-correlation potential. The muffin-tin spheres occupied approximately 60% of the unit cell. The radial parts of the basis functions inside the muffin-tin spheres were calculated from a wave equation for the $l=0$ component of the potential inside the spheres that included mass velocity, Darwin shift, and higher order correc-

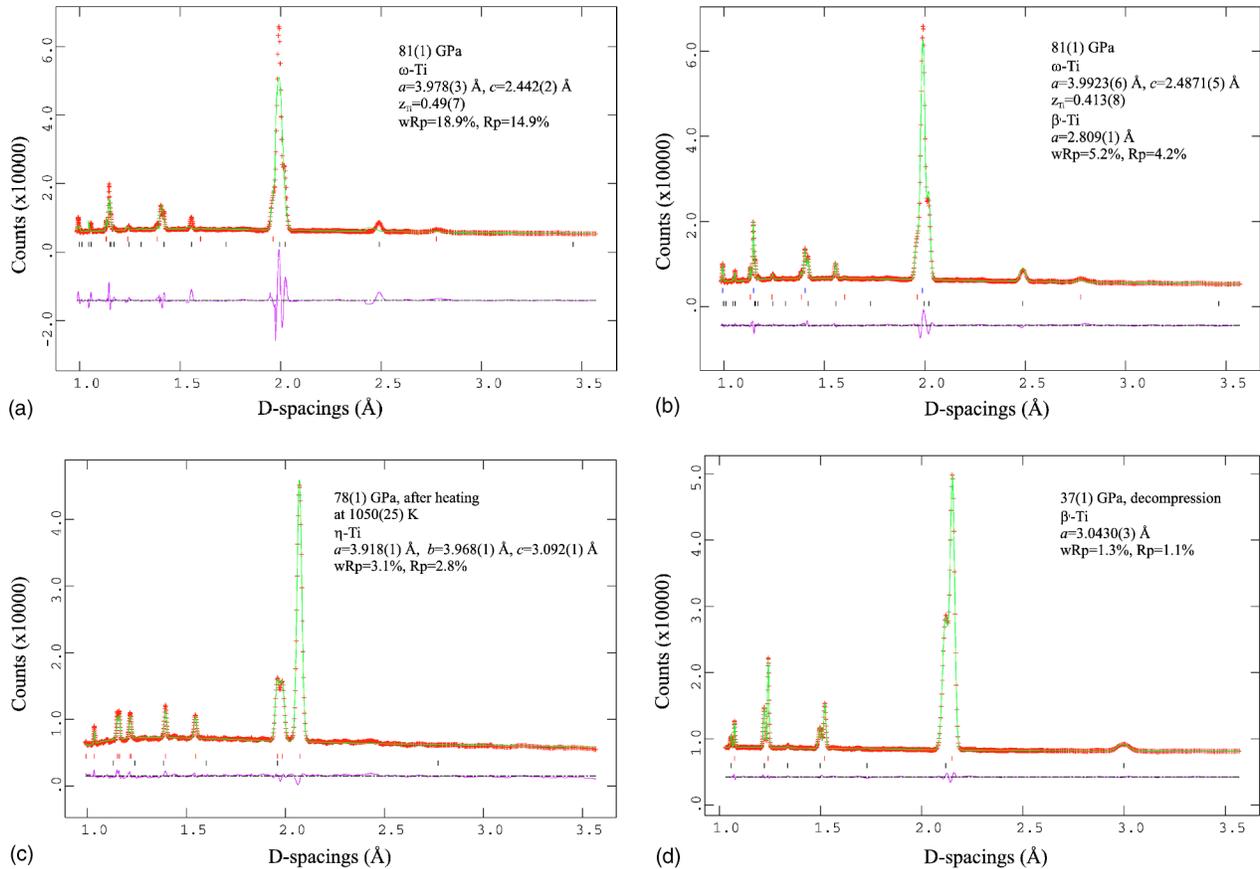


FIG. 3. Examples of a profile-fitted x-ray diffraction pattern obtained in experiments on titanium: (a) data collected at 81(1) GPa and fitted with a mixture of the ω -phase (lower ticks) and B2-NaCl (upper ticks); (b) the same diffraction pattern fitted by a mixture of the ω -phase (lower ticks), B2-NaCl (middle ticks), and β' -Ti (upper ticks); (c) diffraction data from the sample heated during 3 h at 1050(25) K at 78(1) GPa fitted by the orthorhombic (space group $Fm\bar{3}m$) η -Ti structure (upper ticks) (lower ticks-B2-NaCl); (d) diffraction data collected upon decompression of η -Ti at 37(1) GPa and fitted with the bcc-structured β' -Ti (upper ticks) and B2-NaCl (lower ticks).

GPa in terms of just two phases—B2-NaCl (pressure medium) and the ω -Ti [Fig. 3(a)]. At the same time, if we assume that bcc-structured titanium is present in the sample [we will call it β' to underline its structural identity with the low-pressure bcc-titanium (β)], we are able to quantitatively describe the diffraction patterns at pressures up to 80 GPa [Fig. 3(b)].

While heating below 950 K did not result in any noticeable modifications of diffraction patterns, laser-heating at 1200–1300 K or electrical heating at 1050(25) K during 3 h at 78–80 GPa results in significant changes of the diffraction pattern (Fig. 1). Reflections of the new η -phase could be indexed as an orthorhombic lattice and the diffraction pattern could be reproduced by the $Fm\bar{3}m$ space group with Ti in $4a$ (0, 0, 0) position [Fig. 3(c)]. The lattice parameters of η -Ti at 78(1) GPa and ambient temperature are $a=3.918(1)$ Å, $b=3.968(1)$ Å, $c=3.092(1)$ Å. The structure of the η phase could be described as a monoclinically distorted bcc structure with lattice parameters $a'=b'=2.788$ Å, $c=3.092(1)$ Å, $\gamma=89.3^\circ$.

On decompression at room temperature η -Ti transforms into the ideal bcc-structured β' phase at pressures below 40 GPa [Figs. 1 and 3(d)]. Note, that while on compression (or on decompression of the unheated sample) the characteristic

(001) and (111) reflections of ω -Ti are easily detectable, they are absent in the diffraction pattern of the β' -phase obtained by decompression of η -Ti (Fig. 1, inset). On further decompression, at pressures below 30 GPa, β' -Ti transforms to the ω -phase which could be quenched to ambient pressure as was previously observed by Vohra and Spencer.⁴

The compressibility of β' -Ti [$K_T=132(5)$ GPa, $K'=2.4(6)$] is close to the compressibility of ω -Ti [$K_T=126(3)$ GPa, $K'=2.6(4)$ from our data, and $K_T=123.1(4.7)$ GPa, $K'=3.24(1.2)$ according to (5)]. The molar volumes of both β' - and η -Ti are very close to the molar volumes of the ω -phase at corresponding pressure. For example, at 78(1) GPa the molar volume of η -Ti is just $\sim 0.2\%$ lower than the molar volume of ω -Ti. This could explain why (a) the β' - and ω -phases can coexist over such a wide pressure range (at least between 40 and 80 GPa), (b) heating is necessary to activate the transformation from the ω phase to the η phase, and (c) it is so difficult to distinguish the x-ray diffraction patterns of the β' - and ω -phases (at very similar molar volumes the reflections of β' -Ti are just “hidden” under the reflections of ω -Ti).

We have calculated the total energies of the different phases, namely, the ω , γ , δ , η , and β (bcc) phases, as a function of volume for Ti. As an example, in Fig. 4 we show

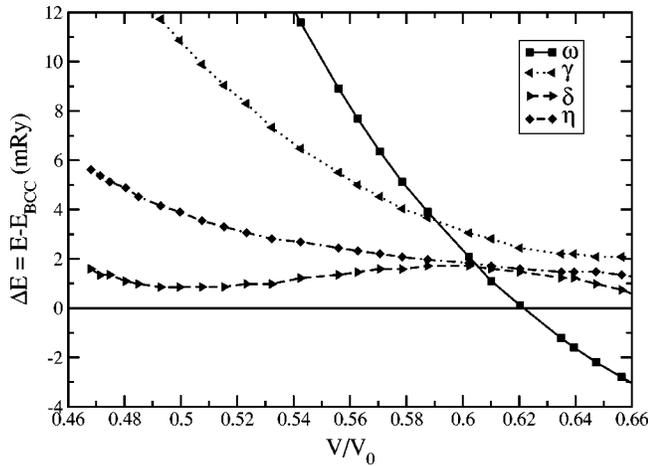


FIG. 4. Total energy differences of Ti as a function of volume (V/V_0 , where V_0 is the experimental volume) for the ω , γ , δ , η , and β (bcc) structures. The total energy of the β (bcc) structure is taken as a reference level.

the differences in total energy as a function of volume, V/V_0 , where V_0 is the experimental equilibrium volume for the hcp phase. In this figure, we have taken the total energy of the bcc phase as a reference level. One can see from Fig. 4 that at compressions down to $V/V_0=0.62$ (pressure about 80 GPa), the ω phase is more stable than the bcc, γ , η , and δ phases. Beyond this compression the bcc phase becomes stable relative to all the other structures. The difference in the total energy between the γ and η phase and the bcc phase increases with decreasing volume, whereas the difference in energy is almost constant in the case of the δ and bcc phase for the studied volume range. Thus our calculations predict that both the γ , η , and δ phases are metastable. In Table I, we have shown our relaxed parameters for the δ , η , and the γ

TABLE I. Calculated structural parameters for the γ and the δ phases along with recent experimental data.

| Structure | Pressure | b/a | c/a | y | |
|-----------------|----------|-------|-------|-------|--------------------|
| γ -phase | 118 GPa | 1.889 | 1.624 | 0.108 | Present Calc. |
| | | 1.878 | 1.639 | 0.100 | Expt. ^a |
| η -phase | 78.0 GPa | 1.007 | 0.704 | ... | Present Calc. |
| | | 1.013 | 0.789 | ... | Present Expt. |
| δ -phase | 178 GPa | 0.716 | 0.989 | 0.268 | Present Calc. |
| | | 0.681 | 0.941 | 0.295 | Expt. ^b |

^aReference 4.

^bReference 5.

phase and compared it with recent experiments. We have also looked into the stability of the γ and δ phase in Zr metal. Again, our calculations do not support the existence of a stable γ and δ phase, which is in agreement with experiment for Zr.

In summary, our experimental and theoretical studies show the existence of the bcc-structure in Ti at high pressure. The transformations in titanium are path-dependent and current experimental information is not sufficient for unambiguous conclusion whether β' -Ti is a stable or metastable phase. Theoretical calculations predict stabilization of bcc-structured titanium at significantly higher pressure (above 80 GPa) than was observed experimentally (above 40 GPa). We have also found that titanium has the potential to form metastable phases (like δ , γ , or η) with very similar molar volumes.

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