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A new distorted body-centred cubic phase of titanium (δ-Ti) at pressures up to 220 GPa

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Abstract

Structural phase transitions of titanium (Ti) have been investigated at pressures up to 220 GPa at room temperature using a monochromatic synchrotron x-ray diffraction technique. At 140 GPa, the hexagonal phase (ω-Ti) was transformed into an orthorhombic phase (δ-Ti) with a distorted bcc structure via an intermediate phase (γ-Ti), which has recently been proposed. The δ-Ti and γ-Ti phases had a unique zigzag-chain-like structure, which resulted from an orthorhombic distortion.

1. Introduction

For titanium (Ti), a 3d transition metal, the hcp phase is stable under ambient conditions. The theoretical analysis by Gyanchandani *et al* [1] has predicted that the hcp (α) phase transforms to the bcc (β) phase at 52–75 GPa via the hexagonal (ω) phase as a result of the s–d transition. Other group IV transition elements, Zr [2–4] and Hf [5, 6], show the same sequence of pressure-induced structural phase transitions: hcp–hexagonal–bcc. The bcc phase is not only found as a high-temperature phase of the group IV transition metals, but also occurs in the group V transition metals, V, Nb and Ta, under ambient conditions. Our previous observation of the relatively high superconducting transition temperature, T_c, of 11 K in bcc-Zr at 31 GPa has provided evidence of a pressure-induced s–d transition in the electronic band structure because the value of T_c is comparable to that (9.2 K) for bcc-Nb at normal pressure [7]. Since the crystal of ω-Ti is a superlattice structure of β-Ti [8], the transition to the bcc phase with higher symmetry with pressure was also expected. However, a previous x-ray study by Xia *et al* [3] reported that ω-Ti is still stable at pressures up to 87 GPa while the α–ω transition occurs at 2 GPa. More recently, a high-pressure phase transition to γ with a distorted hcp structure has been reported by Vohra and Spencer [9]. To clarify the proposed transition to the bcc phase and understand the s–d transition in the 3d electron system, it is essential to research the pressure-induced structural phase transition of Ti to multi-megabar pressures.

In this paper, we present a new structural transition from the hexagonal (ω) phase of Ti to an orthorhombic (δ) phase with a distorted bcc structure at 140 GPa at room temperature via an intermediate phase (γ-Ti).

2. Experimental details

The powder x-ray diffraction profiles were collected by the angle-dispersive method using monochromatic synchrotron radiation sources on BL10XU at SPring-8 [10] and ID30 at ESRF [11]. Several separate experiments were done with different gasket materials or different culet sizes of diamond anvils. A small quantity of the Ti powder with a purity of 99.98% or a Ti foil with a purity of 99.5% was used as the sample. A Pt foil with about 1 μm thickness was used as an internal pressure marker [12]. The estimated standard deviations for the lattice constant of the Pt marker were 0.02–0.03% and the estimated pressure uncertainty was lower than 0.8 GPa at 220 GPa.

3. Results and discussion

The hcp (α) phase of Ti was transformed into the hexagonal (ω) phase with an initial compression to 7.4 GPa. The ω phase was stable up to 124 GPa. At 128 GPa, the ω phase was transformed into the high-pressure phase (γ-Ti). The second transition, reported by Vohra and Spencer [9] as discussed below, was completed at 130 GPa. On further loading to 140 GPa, the intermediate γ phase was transformed to a new high-pressure phase. The transition was also completed at 145 GPa. The highest-pressure phase (δ), with increasing pressure, was stable up to 216 GPa, which is the maximum pressure in the present experiments. The typical profiles of the δ phase at 178 GPa and the γ phase at 130 GPa are shown in figures 1 and 2, respectively. It should be noted that Debye rings from both phases recorded on an image plate showed a preferred orientation effect due to the texture in the sample. When the pressure was released, the δ–γ and γ–ω transitions were observed at 134 and 120 GPa, respectively. Both transitions are reversible with pressure and the coexistence of the δ–γ or γ–ω phases is limited to a narrow pressure region of about 5 GPa.

The diffraction pattern of the δ phase can be indexed on the basis of the orthorhombic lattice shown in figure 1. The lattice parameters at 178 GPa are $a = 3.8610(7)$ Å, $b = 2.6296(6)$ Å and $c = 3.6323(4)$ Å. With the number of atoms in the unit cell $Z = 4$, the atomic volume (9.220 Å^3) is about 5.5% smaller than the extrapolated value, 9.76 Å^3, for the ω phase. These indices showed the systematic absences to be consistent with the space group $Cmcm$ or $Cmc2_1$. The relative intensities were well explained as a $Cmcm$ structure with atoms in the 4c Wyckoff positions $(0, y, 1/4)$, $(0, -y, 3/4)$, $(1/2, y + 1/2, 1/4)$ and $(1/2, 1/2 - y, 3/4)$ with $y = 0.3$ while the 110, 112, 021 and 310 reflection lines disappear with $y = 0.25$. The simulated diffraction pattern is shown by the solid curve in figure 1. This spatial arrangement cannot be distinguished from the 4a positions $(0, y, z)$ and $(0, -y, 1/2 + z)$ of $Cmc2_1$. We assigned this phase to $Cmcm$ as it has a higher symmetry. On the basis of Reitveld refinements of the profile using the computer program REITAN [13], the positional parameter, y, was estimated to be 0.295(5) with an R-factor of $R_{wp} = 12.5\%$ or $R_p = 9.0\%$. The deviation in y from 0.25 leads to a unique zigzag chain structure as mentioned below. The lattice is derived from the bcc structure by means of an orthorhombic distortion. Though the ratios of the lattice parameters, a/b and c/b, are 1.468 and 1.381, respectively, the lattice becomes bcc with $a/b = c/b = \sqrt{2}$ and $y = 0.25$. The structure model is illustrated in figure 3(a).

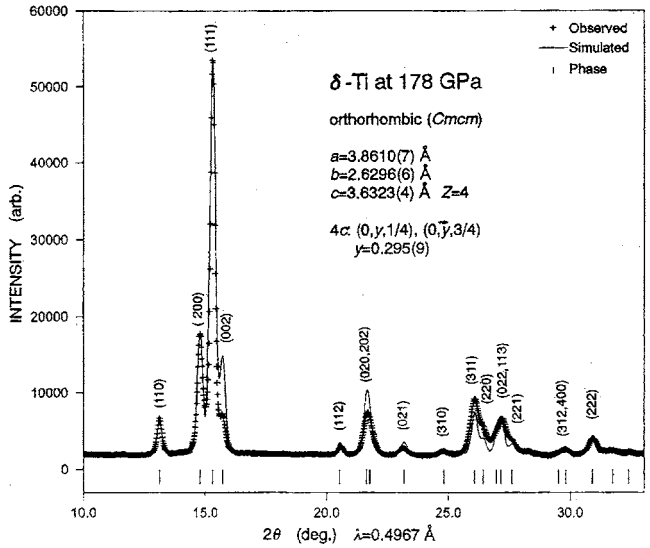

Figure 1. The diffraction profile of the δ phase at 178 GPa.

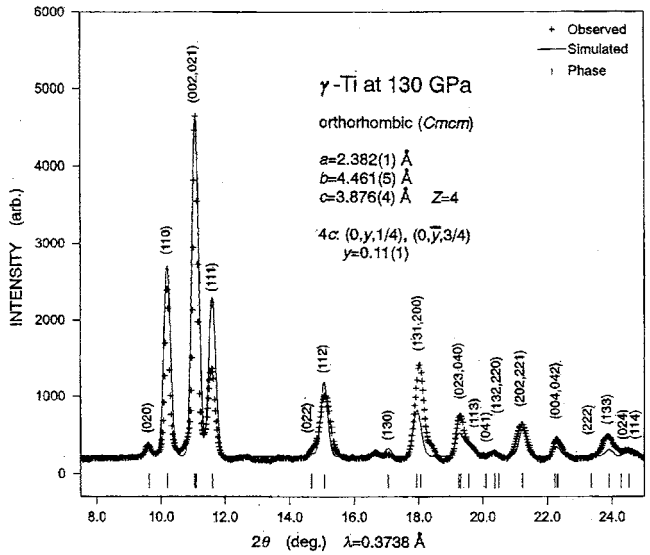

Figure 2. The diffraction profile of the γ phase at 130 GPa.

The second transition at 128 GPa was more recently reported by Vohra and Spencer [9]. The transition pressure is in good agreement with their report, 116 ± 5 GPa, considering the difference in pressure marker: in their experiment, copper was used as the pressure marker. From their diffraction profile with a limited number of diffraction lines (five) and a poor SN ratio, they proposed the intermediate high-pressure phase to be a γ phase with a distorted hcp structure. The proposed structure also belongs to the same orthorhombic lattice, with space group $Cmcm$, and Ti atoms occupy the same 4c positions as in the δ phase. In the present study, the structure of the intermediate γ phase was found by examination to be orthorhombic

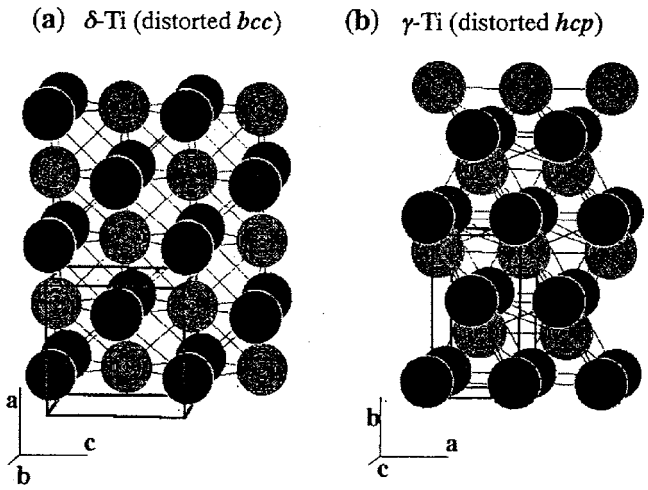

Figure 3. The structure models of the δ and γ phases.

Cmcm, on the basis of the Reitveld refinements. The structure with the lattice and positional parameters of $a = 2.382(1)$ Å, $b = 4.461(5)$ Å and $c = 3.876(4)$ Å and $y = 0.11(1)$ was found to give a calculated intensity in good agreement with the observed data. The simulated profile is also illustrated in figure 2. The atomic volume (10.30 Å^3) is consistent with the pressure versus volume relation (shown in figure 5). The present result agrees with a recent report [9] and the orthorhombic lattice can certainly be described as the distorted hcp structure as shown in figure 3(b).

The most prominent feature of the structures for the δ and γ phases is a unique zigzag chain. The orthorhombic distortion observed in the δ phase splits the isotropic eightfold coordination of the bcc structure. A Ti atom in the δ phase has two nearest-neighbour atoms at the distance of 2.11 Å, four at 2.34 Å and two at 2.39 Å at 178 Pa. Consequently, a zigzag chain structure is formed along the c-axis with a bond angle of 111.8°. The chain structure also exists in the γ phase. As a result of the distortion, the twelvefold coordination in the hcp structure is split into twofold coordination with the distance of 2.17 Å, twofold with 2.38 Å, fourfold with 2.53 Å and fourfold with 2.59 Å at 130 GPa. The zigzag chain also extends along the c-axis with the bond angle of the chain being 120.3°. From the structural models, an orientation relation between the γ and δ phases can be deduced. That is, the three axes, a, b and c, of the γ phase correspond to those of the δ phase.

The γ–δ transition can be interpreted as a drastic rearrangement of the zigzag chains accompanied with contraction of the b-axis and the elongation of the a-axis. Pressure dependences of the lattice parameters for both phases are shown in figure 4. At the γ–δ transition, a shows a large increase from 2.38 to 3.95 Å, while b decreases from 4.4 to 3.6 Å. The a/b and c/b ratios of the δ phase decrease with a weak pressure dependence, but do not go near $\sqrt{2}$ as the pressure changes. The difference between the a/b and c/b ratios is almost constant and there is no sign of a transition to the bcc structure.

The atomic volume, for each phase, is illustrated as a function of pressure in figure 5. The data for the ω phase at ambient pressure are from the results obtained by Jamieson [2]. The data for the ω phase were fitted by the Birch–Murnaghan equation of state [14]. The estimated values for the isothermal bulk modulus at zero pressure, K_0, and its pressure derivative, K_0', were 123.1 ± 4.7 and 3.24 ± 1.2 GPa. From the extrapolation of the equations of state of

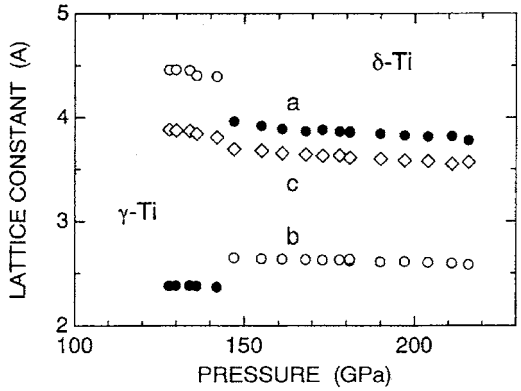

Figure 4. The pressure dependence of the lattice parameters for the δ and γ phases.

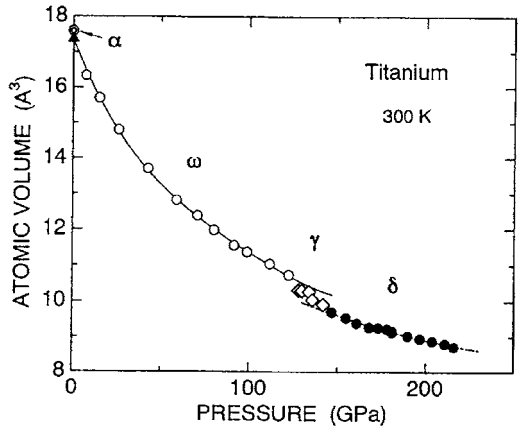

Figure 5. The pressure dependence of the atomic volume for ω-, γ- and δ-Ti.

the ω phase, the volume reduction, $-\Delta V/V$, of the ω–γ phase transition at 130 GPa is 1.6% and that of the γ–δ phase transition at 147 GPa is about 1.4%. The total volume reduction from the ω phase to the δ phase is 3.0% at 147 GPa. This value is comparable to that for the ω–β phase transition of Zr, 2.4% [5]. The volume is finally reduced to 8.711 Å^3 at 216 GPa, our maximum pressure, which corresponds to 0.491 of the volume (17.735 Å^3) of the hcp (α) phase at ambient pressure.

4. Conclusions

Two structural phase transitions were found for the 3d transition metal, Ti, in the megabar pressure region and the structures of two high-pressure phases, δ and γ, were determined and/or confirmed to be orthorhombic $Cmcm$ with distorted bcc and hcp structures, respectively. On the basis of these structural data, we suggested that the two phases consist of a zigzag chain and that a drastic rearrangement of the chains occurs at the γ–δ transition. The observation of the bcc-like δ phase led to the proposed systematic structure sequence of the pressure-induced phase transitions: hcp–hexagonal–bcc for the group IV elements Ti, Zr and Hf.

Acknowledgments

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