New δ (Distorted-bcc) Titanium to 220 GPa

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(Received 7 June 2001; published 10 December 2001)

Structural phase transitions of a 3*d* transition element, titanium, 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 (ω) phase was transformed into an orthorhombic (δ) phase with a distorted bcc structure via an intermediate (γ) phase, which has recently been proposed by Vohra and Spencer [Phys. Rev. Lett. **86**, 3068 (2001)]. Both the δ and the γ phases had a unique zigzag-chain-like structure, which resulted from an orthorhombic distortion. The δ-γ transition could be explained as a rearrangement of the packing between the zigzag chains.

DOI: 10.1103/PhysRevLett.87.275503 PACS numbers: 62.50.+p, 61.50.Ks

Studies of the 3*d* elements at high pressures have attracted special interest because of the electronic-transition induced structural phase transitions, magnetism, and their existence in the earth's core. X-ray structural studies of Mn, Fe, Co, and Ni metals [1–4] have recently been extended to multi-megabar pressures. For transition metals, the phenomenon of electron transfer from the *s* band to the *d* band under pressure (the so-called *s-d* transition) is well known as a common feature of many band structure calculations [5]. It is expected that an increase in the electron number of the *d* band with pressure affects not only the electronic properties but also the stability of the crystal structure. This often induces certain phase transitions because the *d* electrons play a main role in the cohesive mechanism of the transition metals.

For titanium (Ti), a 3*d* transition metal, the hcp phase is stable at ambient conditions. A theoretical analysis [6] has been 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 [7–9] and Hf [10–11], 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 Group V transition metals, V, Nb, and Ta, at 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 the pressure-induced *s-d* transition where the value of T_c is comparable to 9.2 K for bcc-Nb at normal pressure [12]. Since the crystal of ω-Ti is a superlattice structure of β-Ti [13], the transition to the bcc phase with higher symmetry was also expected with pressure. However, a previous x-ray study by Xia *et al.* [8] reported that ω-Ti is still stable at pressures up to 87 GPa while the α-ω transition occurs at 2 GPa. To clarify the proposed transition to the bcc phase and understand the *s-d* transition in the 3*d* electron system, it is essential to research the pressure-induced structural phase transition of Ti to multi-megabar pressures.

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

The powder x-ray diffraction profiles of titanium, in a diamond anvil high-pressure cell (DAC), were collected by the angle dispersive method using a monochromatic synchrotron radiation source ($\lambda = 0.4967$ or 0.3738 Å) on the BL10XU at the Super Photon ring-8 GeV (SPring-8) and the ID30 at the ESRF. Beveled diamond anvils with a center flat size of 75 or 100 μm in diameter with a bevel angle of 8° to 300 μm in culet diameter were used for the pressure generation. A small piece of polycrystalline titanium with a purity of 99.98% was embedded in a hole on a Re metal gasket contained within the DAC, together with a small amount of an internal pressure marker Pt foil with about a 1 μm thickness. The powder profiles were measured up to 216 GPa with an x-ray beam reduced using a pinhole collimator of 20 μm diameter. Pressure was determined from the equation of state of Pt [14]. The estimated standard deviations for the lattice constant of the Pt marker were 0.02–0.03% at pressures up to 216 GPa, and the precision of the estimated pressure was less than 0.8 GPa. In order to avoid the contamination of the diffraction profiles with diffraction lines from the Pt marker, three separate experimental runs were done without the Pt marker. The pressure was then estimated from the pressure dependence of the *d* spacing observed in the first run. One of their runs was carried out with a different gasket material, Udmet700 Ni alloy, in order to check the superposition of the diffraction lines from the Re gasket on those from the sample. The 2θ-intensity profiles were obtained by the integration of the recorded two-dimensional diffraction images [15,16].

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. The profile at 124 GPa is well assigned to the hexagonal lattice with the lattice constants, $a = 3.9038(8)$ and $c = 2.4357(7)$ Å. At 128 GPa, the ω phase was transformed

0031-9007/01/87(27)/275503(4)$15.00

into the high-pressure phase (γ-Ti). The second transition, which has more recently been reported by Vohra and Spencer [17] 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 Figs. 1 and 2, respectively. It should be noted that the 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 the narrow pressure region of about 5 GPa.

The profile of the δ phase can be indexed on the basis of the orthorhombic lattice shown in Fig. 1. The lattice parameters at 178 GPa are $a = 3.8610(7)$, $b = 2.6296(6)$, 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 smaller by about 5.5% than the extrapolated value, 9.76 Å^3, of the ω phase. These indices showed the systematic absences to be consistent with the space groups *Cmcm* or *Cmc*2_1. The relative intensities were well explained as a *Cmcm* structure with atoms in the 4*c* 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 reflection lines of 110, 112, 0.21, and 310 disappear with $y = 0.25$. The simulated diffraction profile is shown by the solid line in this figure. This spatial arrangement cannot be distinguished from the 4*a* positions $(0, y, z)$ and $(0, -y, 1/2 + z)$ of *Cmc*2_1. We assigned this phase to *Cmcm* as it has a higher symmetry. Based on Reitveld refinements of the profile using the computer program REITAN [18], the positional parameter, y, was estimated to be 0.295(5) with an R factor of $R_{wp} = 12.5\%$ (or $R_p = 90\%$). The deviation in y from 0.25 results in 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 Fig. 3(a). The relative intensity of the profile was almost independent of pressure.

The second transition at 128 GPa has more recently been reported by Vohra and Spencer [17]. The transition pressure is in good agreement with their report, 116 ± 5 GPa, considering the difference in the pressure marker which was copper in their study. They have proposed from a diffraction profile with only five diffraction lines and a poor SN ratio that the intermediate high-pressure phase was assigned to the γ phase with a distorted hcp structure. The proposed structure also belongs to the same orthorhombic lattice, space group: *Cmcm*, and Ti atoms also occupy the same 4*c* positions as for the δ phase. In the present study, the structure of the intermediate γ phase was examined to be orthorhombic *Cmcm* based on the Reitveld refinements. The structure with the lattice and positional parameters of $a = 2.382(1)$, $b = 4.461(5)$, $c = 3.876(4)$ Å, and $y = 0.11(1)$ was found to give a calculated intensity

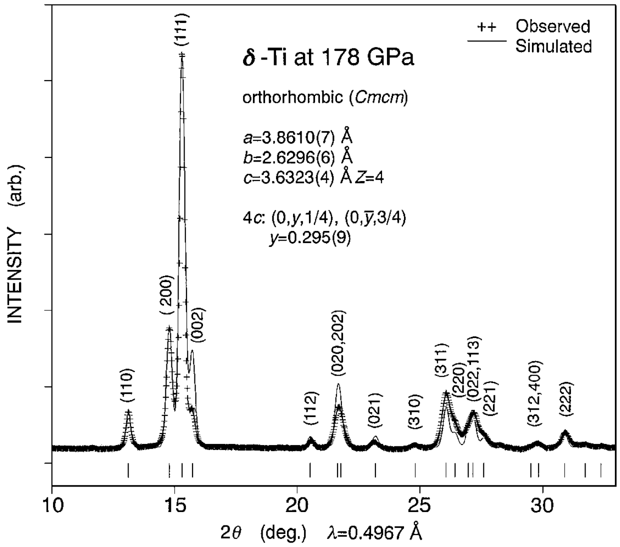

FIG. 1. The diffraction profile of δ-Ti at 178 GPa. The profile is indexed on the basis of the orthorhombic *Cmcm* lattice. The solid line represents a simulated pattern for the orthorhombic structure with the lattice parameters, a, b, and c, and the position, y, shown in the figure.

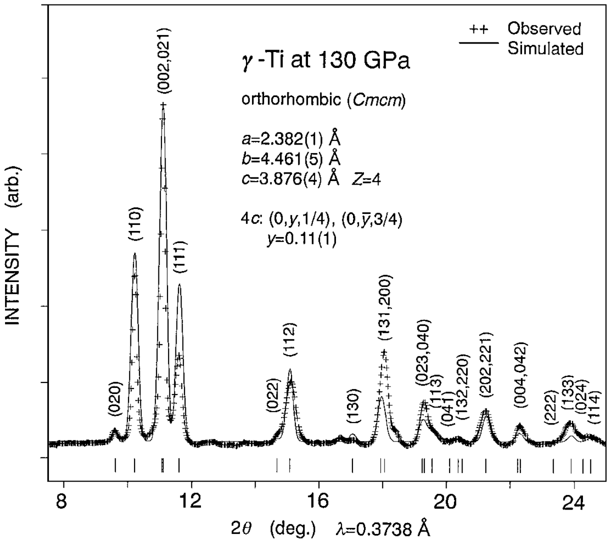

FIG. 2. The diffraction profile of γ-Ti at 130 GPa. The profile is indexed on the basis of the orthorhombic *Cmcm* lattice.

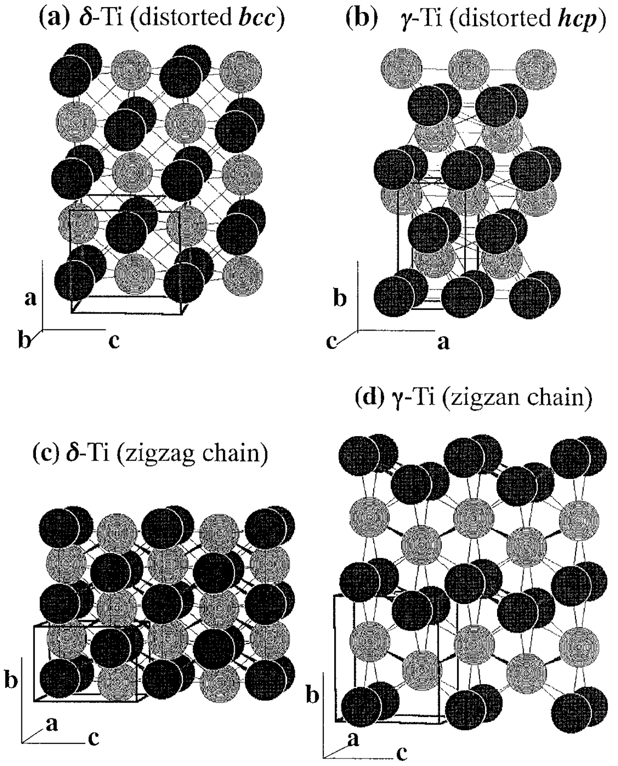

FIG. 3. Structure models of the δ and the γ phases. (a) and (b) correspond to the δ and the γ phases, respectively. In (a), the lattice is described as a distorted bcc structure, and atoms shown by gray correspond to the body-center site. In (b), the lattice is also as a distorted hcp structure. The hexagonal plane corresponds to the *ab* plane, and atoms shown by black and gray represent the ABAB stacking of the hexagonal plane along the *c* axis. (c) and (d) illustrate zigzag-chain structures of the δ and the γ phases, respectively. The zigzag chains extended along the *c* axis in both phases. From the figures, we can find the orientation relation between δ and the γ phases; namely, three axes, *a*, *b*, and *c*, of the γ phase correspond to those of the δ phase.

in good agreement with the observed data. The simulated profile is illustrated in Fig. 2. The atomic volume (10.30 Å^3) is consistent with the pressure vs volume relation [shown in Fig. 5 (below)]. The present result agrees with a recent report [17], and the orthorhombic lattice is certainly described as the distorted hcp structure as shown in Fig. 3(b). The *Cmcm* structure has been reported in the tetravalent III-V and II-VI binary semiconductors as high-pressure phases [19], while we do not know of their existence in monatomic systems.

The most prominent feature of the structures for the δ and the γ phases is a unique zigzag-chain-like structure, which is illustrated in Figs. 3(c) and 3(d), respectively. The orthorhombic distortion observed in the δ phase splits the isotropic eightfold coordination of the bcc structure as shown in Fig. 3(c). A Ti atom in the δ phase has two nearest neighbor atoms with the distance of 2.11 Å, four with 2.34 Å, and two with 2.39 Å at 178 GPa. 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. By the distortion, the 12-fold coordination in the hcp structure is split into twofold coordination with the distance of 2.17 Å, two with 2.38 Å, four with 2.53 Å, and four 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 the δ phases can be deduced. Namely, the three axes, *a*, *b*, and *c*, of the γ phase correspond to those of the δ phase.

The γ-δ transition can be described 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 Fig. 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 2.6 Å. The lattice deformation could also be interpreted by means of the Burgers mechanism of the martensitic transition between the hcp and the bcc structures [20]. We should note that, in such a transition, the dynamical evolution would be affected by the lattice strain due to the nonhydrostatic condition. The a/b and c/b ratios of the δ phase decrease with a weak pressure dependence but do not go near $\sqrt{2}$ with pressure. The difference between the a/b and c/b ratios is almost constant, and any sign for the transition to the bcc structure is not observed in these results. Lattice constants, *a* and *c*, and the c/a ratio of the ω phase are consistent with the recent result [17]. The anisotropy of lattice compression is observed at lower pressures. The ratio increases with pressure from 0.608 at

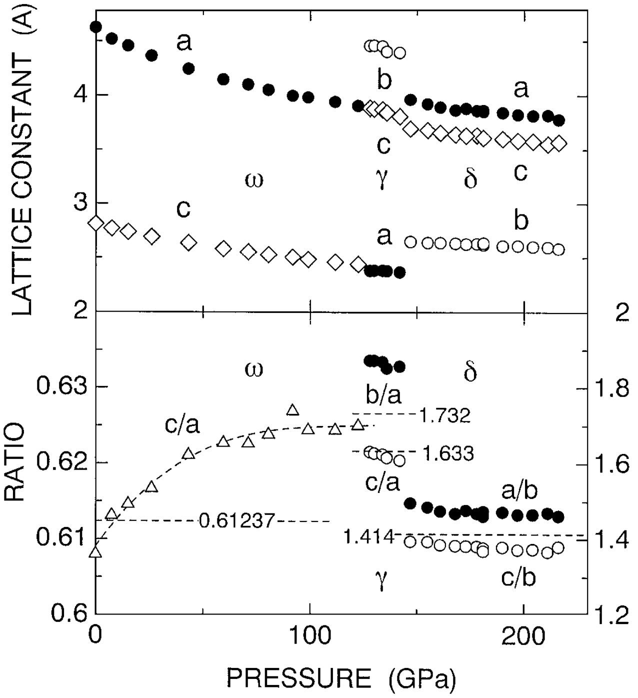

FIG. 4. The pressure dependence of the lattice parameters and their ratios for the ω, δ, and γ phases.

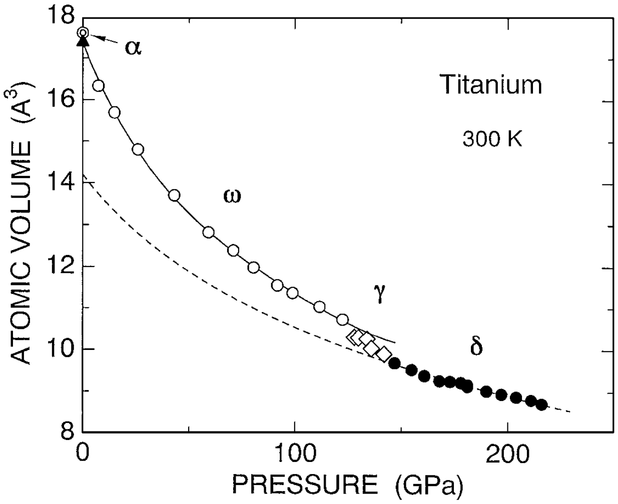

FIG. 5. The pressure dependence of atomic volume for the ω, γ, and δ phases of Ti. The data at ambient pressure is from the result by Jamieson [7]. The solid line represents the result of a least-squares fit of the Birch-Murnaghan equation of state to the data of the ω phase, $B_0 = 123.1 \pm 4.7$ GPa and $B_0' = 3.24 \pm 1.2$. The broken line shows the pressure-volume relation of the δ phase, which can be represented by the equation with $B_0 = 211.2 \pm 2.8$ GPa, $B_0' = 3.24$ (fixed), and $V_0 = 14.20 \pm 0.04$ Å^3.

zero pressure to 0.625 at 100 GPa, though the ideal ratio of the ω phase is equal to 0.612. The ratio above 100 GPa is independent of pressure.

The atomic volume of each phase is illustrated as a function of pressure in Fig. 5. The data of the ω phase were fitted by the Birch-Murnaghan equation of state [21],

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

where $x = V_0/V$, V is the volume per Ti atom, and V_0 (17.37 Å^3) is the atomic volume of the ω phase at zero pressure. B_0 is the isothermal bulk modulus at zero pressure, and B_0' is the pressure derivative of B_0. The estimated values for B_0 and B_0' were 123.1 ± 4.7 GPa and 3.24 ± 1.2. From the extrapolation of the equations of state of 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 to the δ phase is 3.0% at 147 GPa. This value is comparable to that of the ω-β phase transition of Zr, 2.4% [9]. 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. The atomic volume is greater by 20% than those of the other 3d transition metals at 200 GPa, i.e., Mn(7.45 or 7.31 Å^3) [1], Fe(7.47 Å^3) [2], Co(7.40 Å^3) [3] and Ni(7.39 Å^3) [4].

In conclusion, two structural phase transitions were found for the 3d transition metal, titanium, 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. Based on these structural data, we suggested that the two phases consisted of a zigzag chain and a drastic rearrangement of the chains, which occurs at the γ-δ transition. The observation of the bcc-like δ phase revealed the proposed systematic structure sequence of the pressure-induced phase transitions; hcp-hexagonal-bcc in the Group IV elements, Ti, Zr, and Hf. The formation of the zigzag chain was caused by the orthorhombic distortion. Since such a distortion has not been observed in other 3d transition elements under high pressure, it should be caused by the tetravalent 3d electronic band structure.

This work was supported by a Grant-in-Aid for Scientific Research (C) (Grant No. 12640321) from the Japan Society for the Promotion of Science, and performed under Proposals No. 1999B0107-CD-np, No. 2000A0174-ND-np, and No. 2000B0178-CD-np at SPring-8.

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