

# Neutron and X-ray Diffraction Study on the Location of Hydrogen Isotopes in TiO<sub>0.3</sub> and ZrO<sub>0.4</sub>

著者	Kajitani T., Mukawa S., Hirabayashi M.
journal or publication title	Materials Transactions, JIM
volume	32
number	9
page range	807-813
year	1991
URL	<a href="http://hdl.handle.net/10097/52062">http://hdl.handle.net/10097/52062</a>

# Neutron and X-ray Diffraction Study on the Location of Hydrogen Isotopes in $\text{TiO}_{0.3}$ and $\text{ZrO}_{0.4}$

T. Kajitani\*, S. Mukawa\*<sup>†</sup> and M. Hirabayashi\*<sup>††</sup>

The purpose of the present work is to determine the hydrogen trapping sites in the title oxides which can store relatively large amount of hydrogen isotopes. Neutron inelastic down scattering spectra are obtained for the hydrogenated samples in the energy range up to 15 kJ/mol to determine the hydrogen local vibration energy eigenvalues from which we can guess whether hydrogen atoms are trapped in the tetrahedral interstices or in the octahedral ones. An iterative calculation is done for the obtained neutron inelastic scattering spectra. The energy eigenvalues and the amplitudes of each hydrogen vibration mode are determined considering the local symmetry of the interstices.

X-ray and neutron single-crystal diffraction measurements are carried out for the deuterium charged samples. Conventional structural analyses i.e. the least squares calculation are done for two sets of X-ray and neutron diffraction data taken from  $\text{TiO}_{0.3}\text{D}_{0.1}$  and  $\text{ZrO}_{0.4}\text{D}_{0.1}$  samples for which the space symmetry of the trigonal P31m- and P312-types are assigned, respectively. Deuterium atoms occupy octahedral interstices in  $\text{TiO}_{0.3}\text{D}_{0.1}$  but occupy tetrahedral ones in  $\text{ZrO}_{0.4}\text{D}_{0.1}$ . Arrangements of oxygen atoms have been described as the regular stacking order similar with those of  $\alpha'$ - $\text{TiO}_x$  with  $x < 0.5$  and  $\alpha''$ - $\text{ZrO}_z$  with  $z < 0.4$  types, respectively.

(Received April 8, 1991)

**Keywords:** hydrogen, deuterium, titanium, zirconium, oxide, neutron inelastic scattering, X-ray diffraction, neutron diffraction

## I. Introduction

Research effort was focused on the site location of hydrogen isotopes and chemical interactions between oxygen and hydrogen isotopes in hexagonal titanium or zirconium lattice. The location sites of hydrogen isotopes in the  $\alpha$ - $\text{ZrH}(\text{D})_x$  ( $x < 0.05$ ) were found at T-sites by Narange *et al.*<sup>(1)</sup>, Khoda-Bakhoh *et al.*<sup>(2)</sup>, Hempelmann *et al.*<sup>(3)</sup> by means of the neutron diffraction or neutron inelastic scattering measurements. The energy eigenvalues of hydrogen and deuterium local modes in the  $\alpha$ - $\text{ZrH}(\text{D})_x$  were obtained respectively at 13.9 and 10.2 kJ/mol (144 and 106 meV), which are at typical levels for the T-site occupancy by Khoda-Bakhoh and Ross<sup>(2)</sup>. Present authors<sup>(4)</sup> previously found that energy eigenvalues of the hydrogen local modes in the  $\text{ZrO}_{0.4}\text{H}_{0.1}$  at 13.0 kJ/mol (135 meV) with FWHM at 2.0 kJ/mol (21 meV) by means of the neutron inelastic scattering measurement. This energy eigenvalue is at a reasonable level for hydrogen atoms located at T-sites.

On the other hand, the site location of hydrogen isotopes in the  $\alpha$ - $\text{TiH}(\text{D})_x$  ( $x < 0.09$ ) were controversial. Low solubility limit on the  $\alpha$ - $\text{TiH}(\text{D})_x$  caused some difficulty in the interpretation of obtained neutron inelastic scattering spectrum at temperatures below 473 K. Hempelmann *et al.*<sup>(3)</sup> found inelastic peaks at 14.6 and 10.2 kJ/mol (151 and 106 meV) in  $\text{TiH}_{0.07}$  at 298 and 599

K, respectively. Those values may indicate that hydrogen atoms are trapped at T-sites of  $\gamma$ - $\text{TiH}_2$  precipitates at 298 K but the precipitates are resolved at 599 K. The trapping sites may be changed to O-sites at 599 K.

The present work was aimed to determine the structural parameters of the  $\text{TiO}_{0.3}\text{D}_{0.1}$  and  $\text{ZrO}_{0.4}\text{D}_{0.1}$  by means of X-ray and neutron single-crystal diffraction measurements. Also, the energy eigenvalues of the hydrogen local mode in the  $\text{TiO}_{0.3}\text{H}_{0.1}$  was measured to obtain invaluable insight of the hydrogen isotope trapping sites. In the present work, detailed structural analysis is carried out on the  $\text{ZrO}_{0.4}\text{D}_{0.1}$  previously studied by means of the TOF-type neutron diffraction measurement<sup>(4)</sup>. The neutron inelastic scattering data on the  $\text{ZrO}_{0.4}\text{H}_{0.1}$  obtained previously<sup>(4)</sup> are re-analyzed carefully in the present work. Figures 1 and 2 show Ti-O-H and Zr-O-H ternary phase diagrams determined by Yamaguchi<sup>(5)</sup> and Jostsons *et al.*<sup>(6)</sup> for the Ti-O-H system and Hirabayashi *et al.*<sup>(7)</sup> and Ells *et al.*<sup>(8)</sup> for the Zr-O-H system. Based on the structural model, it is expected that the highest hydrogen concentration is 30 at% at about the same temperature in the Ti-O-H system. In the case of the Zr-O-H system, hydrogen may be store up to 25 at% at the oxygen concentration of about 20 at% at 1023 K.

The phase diagram of the Ti-O system<sup>(5)(9)-(13)</sup> has close resemblance with that of the Zr-O system. There are  $\alpha$ -,  $\alpha'$ - and  $\alpha''$ -phases<sup>(13)</sup> in the oxygen concentration range  $\text{O}/\text{Ti} < 0.5$ . The  $\alpha$ -phase is a high temperature disordered phase in which oxygen atoms site at O-sites. The  $\alpha'$ -phase exist at temperatures higher than 723 K. This phase is a trigonal phase<sup>(5)</sup> with a space symmetry of P3m1-type (No. 164), in which the O-site layers are alternatively occupied by oxygen atoms along the *c*-axis. Yamaguchi,

\* Institute for Materials Research, Tohoku University, Sendai 980, Japan.

<sup>†</sup> Present address: Nippon Steel Co., Tokai 476, Japan.

<sup>††</sup> Present address: Kitami Institute of Technology, Kitami, Hokkaido 090, Japan.

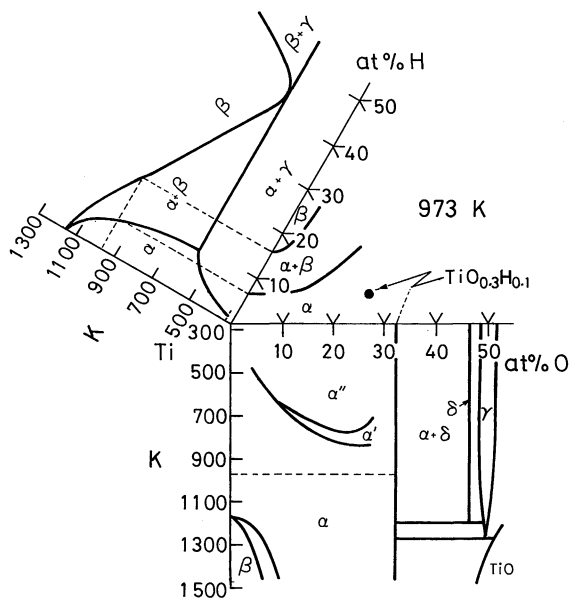


Fig. 1 Partial phase diagram of Ti-O-H, Ti-H and Ti-O.

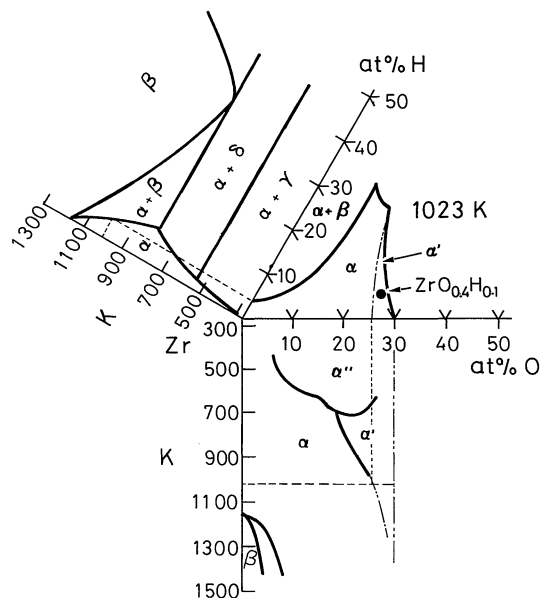


Fig. 2 Partial phase diagram of Zr-O-H, Zr-H and Zr-O.

Koiwa and Hirabayashi<sup>(5)(7)(13)</sup> found that there are three types of  $\alpha''$ -phases, namely I-, II- and III-types. The difference between the three comes from the ordered arrangements of oxygen atoms.

According to literatures<sup>(7)(14)-(19)</sup>, there are five different kinds of hexagonal or trigonal  $ZrO_x$  ( $x < 0.5$ ) at temperatures below 723 K, namely  $\alpha$ - $ZrO_x$  ( $x < 0.5$ ),  $\alpha'$ - $ZrO_y$  ( $0.3 < y < 0.5$ ),  $\alpha''$ - $ZrO_x$  ( $x < 0.3$ ), long period- $ZrO_u$  ( $u - 1/3$ ) and  $\alpha''$ - $ZrO_z$  ( $z - 0.4$ ). These phases are designated by the stacking orders of oxygen atoms located in octahedral interstices. The superstructure of the  $\alpha''$ - $ZrO_z$ , which is the matrix of present  $ZrO_{0.4}D_{0.1}$  sample, is described by Hashimoto<sup>(18)</sup> as a defective structure of the  $\epsilon$ - $Fe_2N$  type, which has the space symmetry of P312-type.

## II. Experimental

$TiO_{0.3}$  and  $ZrO_{0.4}$  powder and single crystals were prepared from ingots which were repeatedly molten in an argon-arc-furnace as being described elsewhere<sup>(20)</sup>. Hydrogen and deuterium gas were charged by a Sieverts-type apparatus. A time-of-flight-type neutron inelastic scattering measurement<sup>(21)</sup> was done to determine the energy eigenvalues of hydrogen local vibration modes in the  $TiO_{0.3}H_{0.1}$  and the  $ZrO_{0.4}H_{0.1}$ . Powder samples were sealed in a flat aluminum cassette ( $85 \times 110 \times 3$  mm<sup>3</sup>). The instrumental energy resolution at about 9.65 kJ/mol (100 meV) is 3.9 kJ/mol (4 meV). The density of states,  $Z(\omega)$ , of local hydrogen modes and the average thermal vibration amplitudes  $\langle u^2 \rangle$  of a hydrogen atom are obtained from the inelastic scattering spectra.

RIGAKU-AF3 automated four-circle X-ray diffractometer was used with monochromatized Mo- $K\alpha$  radiation. A 0.5 mm $\phi$  divergence collimator and a 5.5 mm slit were used. The KID neutron diffractometer in JAERI was utilized with a four-circle goniometer with monochromatized neutron beam of  $\lambda = 102$  pm. The collimation of 15'-hole-30' from the monochromator through the neutron counter was kept during the measurement.

Integrated intensities of 612 and 756 non-zero Bragg-reflections obtained at room temperature by the X-ray diffraction at the scattering angles,  $2\theta$ , more than  $60^\circ$  are analyzed for the  $TiO_{0.3}D_{0.1}$  and  $ZrO_{0.4}D_{0.1}$ , respectively. The integrated X-ray intensities obtained in the range of  $2\theta < 60^\circ$  are discarded because of possible overlapping<sup>(18)</sup> of neighboring Bragg-reflections. 120 and 47 integrated neutron Bragg-intensities were measured for the two crystals, respectively. The  $\theta$ - $2\theta$  scan-mode was kept throughout the X-ray and neutron diffraction works.

The lattice parameters were calculated from 16~24 sets of reflection indices and scattering angles measured by the X-ray diffraction by the Bond method at the scattering angles about  $60^\circ$ . The full matrix least squares calculation computer program RADIEL developed by Coppens *et al.*<sup>(22)</sup> was utilized to determine the structural parameters. Integrated intensities of X-ray and neutron diffractions were analyzed self-consistently and simultaneously.

## III. Hydrogen Local Modes in $TiO_{0.3}H_{0.1}$ and $ZrO_{0.4}H_{0.1}$

Figures 3 and 4 show the density of state curves of hydrogen local modes in the  $TiO_{0.3}H_{0.1}$  and previously obtained curve in the  $ZrO_{0.4}H_{0.1}$ . The energy eigenvalues at the maximum point of the density of state curves are 9.2 and 12.9 kJ/mol (95 and 134 meV) for the  $TiO_{0.3}H_{0.1}$  and  $ZrO_{0.4}H_{0.1}$ <sup>(4)</sup>, respectively. The former and the latter values are at the typical local vibration-mode-levels of the hydrogens trapped at octahedral and tetrahedral interstices, respectively. The density of state curves were separated into subpeaks which correspond to a single- and double-degenerated modes i.e. a singlet and a

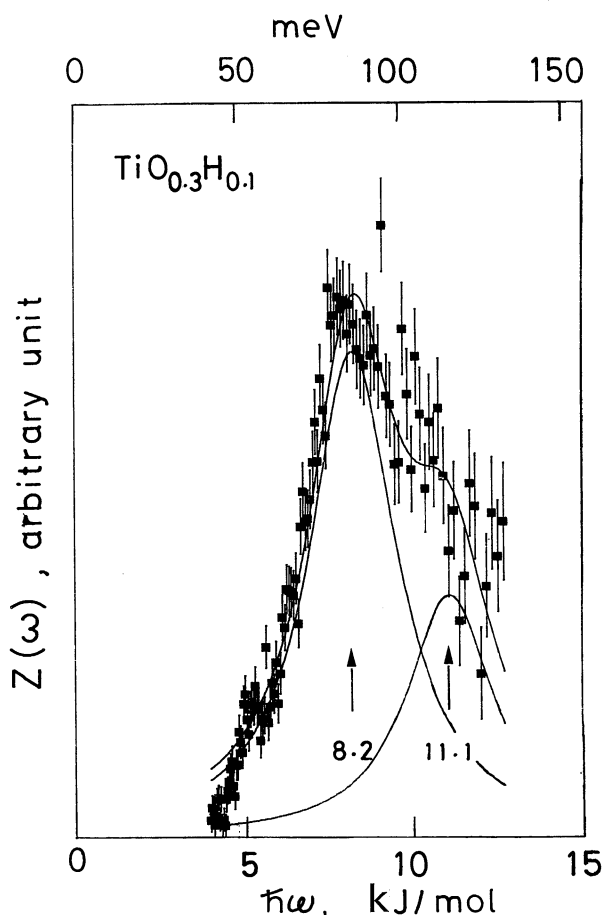


Fig. 3 Density of state curve,  $Z(\omega)$ , of hydrogen local modes in the  $\text{TiO}_{0.3}\text{H}_{0.1}$  lattice. Two Lorentz type peaks, which stand at the energy values 8.2 and 11.1 kJ/mol (85 and 115 meV), correspond to the doublet and the singlet, respectively.

doublet in both systems. For each inelastic subpeak, a Lorentz-type resolution function, i.e.

$$f(h\omega) = (1/2\Gamma)^2 / \{(\hbar\omega - \hbar\omega_1)^2 + (1/2\Gamma)^2\},$$

was assigned, where  $\Gamma$ ,  $\hbar\omega$  and  $\hbar\omega_1$  are the FWHM, energy transfer and energy eigenvalue, respectively. The calculation was done in an iterative method described previously<sup>(23)</sup>.

The least-squares method was adopted to obtain most suitable  $\Gamma$ ,  $\omega_1$  and peak height for the singlet and the doublet peaks. Table 1 shows determined energy eigenvalues and FWHM. The singlet and the doublet in the  $\text{TiO}_{0.3}\text{H}_{0.1}$  have the energy eigenvalues at 11.1 and 8.2 kJ/mol (115 and 85 meV) with the FWHM of 3.1 kJ/mol (32 meV). From these energy eigenvalues, we may assume that hydrogen atoms are trapped in O-sites. Due to local symmetry at the O-sites, the singlet and the doublet correspond to a vertical (parallel to the  $c$ -axis) and a horizontal (perpendicular to the  $c$ -axis) vibration modes, respectively.

Similar calculation was carried out for the neutron inelastic scattering data of  $\text{ZrO}_{0.4}\text{H}_{0.1}$ . Occupation of T-sites by hydrogen atoms was found previously<sup>(4)</sup>. In the  $\text{ZrO}_{0.4}\text{H}_{0.1}$ , also the singlet should have lower energy

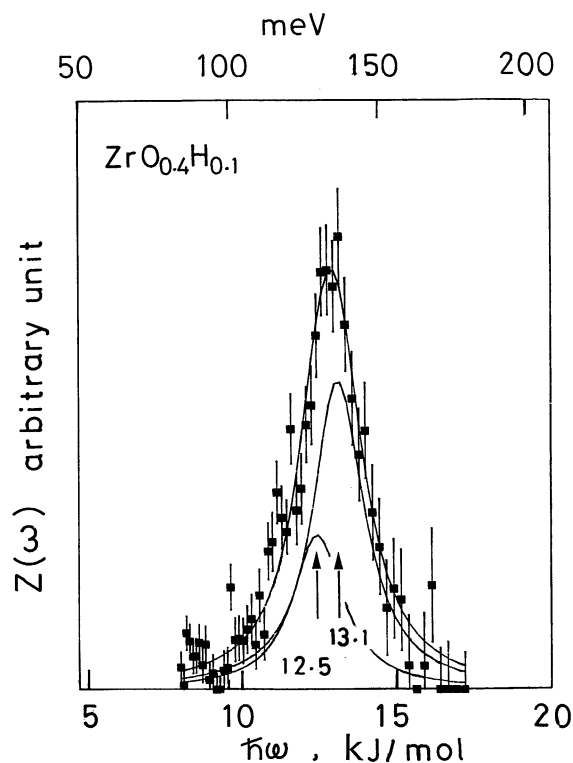


Fig. 4 Density of state curve,  $Z(\omega)$ , of hydrogen local modes in the  $\text{ZrO}_{0.4}\text{H}_{0.1}$  lattice. Experimentally obtained curve was fitted with two Lorentz type peaks which have identical FWHM.

Table 1 Energy eigenvalues of hydrogen local modes in the  $\text{TiO}_{0.3}\text{H}_{0.1}$  and  $\text{ZrO}_{0.4}\text{H}_{0.1}$ .

Specimen	Energy kJ/mol	Singlet	Doublet	FWHM
$\text{TiO}_{0.3}\text{H}_{0.1}$	14.5	8.2	3.1	
$\text{ZrO}_{0.4}\text{H}_{0.1}$	12.5	13.1	2.7	

eigenvalue than the doublet because of the local symmetry at T-sites. After the iterative calculation, it is concluded that the singlet-vertical-mode and the doublet-horizontal-mode have energy eigenvalues at 12.4 and 13.1 kJ/mol (129 and 136 meV) with the FWHM of 2.1 kJ/mol (20 meV). The ratio of the integrated intensities of the singlet and the doublet becomes about 1/2, being quite reasonable.

The mean squares displacement  $\langle u^2 \rangle$  of hydrogen atoms becomes 400 and 600 pm<sup>2</sup> ( $B=31600$  and 47400 pm<sup>2</sup>) for the  $\text{TiO}_{0.3}\text{H}_{0.1}$  and  $\text{ZrO}_{0.4}\text{H}_{0.1}$ , respectively.

#### IV. Crystal Structure of $\text{TiO}_{0.3}\text{D}_{0.1}$

Determined structural parameters of the  $\text{TiO}_{0.3}\text{D}_{0.1}$  are listed in Table 2. The space symmetry of the  $\text{TiO}_{0.3}\text{D}_{0.1}$  has been designated as the same type of P31m (No. 157) while the  $\alpha'$ - $\text{TiO}_x$  ( $x < 0.5$ ) has the space symmetry of P3m1 (No. 164)-type. Figure 5 shows the crystal structure of the  $\text{TiO}_{0.3}\text{D}_{0.1}$ . The length of  $c$ -axis is one half as

Table 2 Determined structural parameters of the  $\text{TiO}_{0.3}\text{D}_{0.1}$  and  $\text{ZrO}_{0.4}\text{D}_{0.1}$ .

	$\text{TiO}_{0.3}\text{D}_{0.1}$	$\text{ZrO}_{0.4}\text{D}_{0.1}$
Symmetry	Trigonal P31m (No. 157)	Trigonal P312 (No. 149)
Lattice constants (pm)	515.8(4) 515.8(4) 481.2(3)	563.28(5) 563.28(5) 522.10(7)
Ti(1); $3c(x\ 0\ z)$ $x=0.3403(13)$ $z=0.2299(4)$ $u_{11}=110.4(52)\ \text{pm}^2$ $u_{22}=109.4(53)\ \text{pm}^2$ $u_{33}=184.6(62)$ $u_{12}=54.7(52)$ $u_{13}=22.3(35)$ $u_{23}=0$ $B=14696$	Zr; $6l(x\ y\ z)$ $x=0.3329(2)$ $y=-0.0006(2)$ $z=0.2500(1)$ $u_{11}=31.3(9)$ $u_{22}=31.3(9)$ $u_{33}=0.1(15)$ $u_{12}=14.4(9)$ $u_{13}=0(2)$ $u_{23}=0(3)$ $B=2408$	
Ti(2); $3c(x\ 0\ z)$ $x=0.6667(15)$ $z=0.7279(4)$ $u_{11}=5.2(34)$ $u_{22}=5.2(34)$ $u_{33}=5.9(35)$ $u_{12}=2.6(34)$ $u_{13}=1.3(23)$ $u_{23}=1.3(23)$ $u_{23}=0$ $B=634$		
O(1); $2b(1/3\ 2/3\ z)$ $z=0.4443(34)$ $\text{occ}=0.42(3)$ $u_{11}=u_{22}=93(53)$ $u_{33}=49(55)$ $u_{12}=47(53)$ $u_{13}=u_{23}=0$ $B=4974$	O(1); $1f(2/3\ 1/3\ 1/2)$ $\text{occ}=1.00(8)$ $u_{11}=u_{22}=78(69)$ $u_{33}=57(51)$ $u_{12}=39(69)$ $u_{13}=u_{23}=0$ $B=7659$	
O(2); $1a(0\ 0\ z)$ $z=0.4443(65)$ $\text{occ}=0.43(3)$ $u_{11}=u_{22}=93(110)$ $u_{33}=49(106)$ $u_{12}=47(102)$ $u_{13}=u_{23}=0$ $B=4974$	O(2); $1d(1/3\ 2/3\ 1/2)$ $\text{occ}=0.54(7)$ $u_{11}=u_{22}=90(108)$ $u_{33}=57(72)$ $u_{12}=45(107)$ $u_{13}=u_{23}=0$ $B=8606$	
O(3); $2b(1/3\ 2/3\ z)$ $z=0.0$ $\text{occ}=0.20(2)$ $u_{11}=u_{22}=18(94)$ $u_{33}=14(95)$ $u_{12}=9(94)$ $u_{13}=u_{23}=0$ $B=1789$	O(3); $1a(0\ 0\ 0)$ $\text{occ}=1.00(7)$ $u_{11}=u_{22}=83(62)$ $u_{33}=67(44)$ $u_{12}=42(62)$ $u_{13}=u_{23}=0$ $B=8343$	
O(4); $1a(0\ 0\ z)$ $z=0.0$ $\text{occ}=0.19(4)$ $u_{11}=u_{22}=18(194)$ $u_{33}=14(199)$ $u_{12}=9(197)$ $u_{13}=u_{23}=0$ $B=1789$		
D(1); $2b(1/3\ 2/3\ z)$ $z=0.0$ $\text{occ}=0.19(3)$ $u_{11}=300(200)$ $u_{33}=200(200)$ $u_{12}=200(200)$ $u_{13}=u_{23}=0$ $B=31600$	D(1); $6l(x\ y\ z)$ $x=0.341(84)$ $y=-0.018(120)$ $z=0.537(39)$ $\text{occ}=0.04(1)$ $u_{11}=400(200)$ $u_{22}=200(800)$ $u_{33}=200(800)$ $u_{13}=0(100)$ $u_{23}=0(80)$ $B=36800$	

D(2); $1a(0\ 0\ z)$ $z=0.0$ $\text{occ}=0.18(7)$ $u_{11}=u_{22}=300(500)$ $u_{33}=200(400)$ $u_{12}=200(500)$ $u_{13}=u_{23}=0$ $B=31600$	D(2); $6l(x\ y\ z)$ $x=0.669(53)$ $y=0.057(58)$ $z=0.113(14)$ $\text{occ}=0.06(4)$ $u_{11}=400(800)$ $u_{22}=400(900)$ $u_{33}=200(200)$ $u_{12}=200(700)$ $u_{13}=0(800)$ $u_{23}=0(400)$ $B=36800$	
Residuals	X-ray neutron	X-ray neutron
$R_f$	0.1023 0.1498	0.0766 0.1122
$R_w$	0.0991 0.1354	0.0537 0.0819
Reflections	612 120 ( $2\theta > 66^\circ$ )	756 47 ( $2\theta > 60^\circ$ )
Wave length (pm)	70.92 101.9 (Mo-K $\alpha$ )	70.92 101.9 (Mo-K $\alpha$ )
Chemical	$\text{TiO}_{0.307}\text{D}_{0.092}$	$\text{ZrO}_{0.423}\text{D}_{0.099}$

long as that of the  $\alpha''$ - $\text{TiO}_{0.3}$  for which the space symmetry of P31c(No. 163) type was assigned by Yamaguchi *et al.*<sup>(5)</sup>. It was noted that no type-II but types-I and -III Bragg reflection was observed by X-ray and neutron diffraction for the  $\text{TiO}_{0.3}\text{D}_{0.1}$ . The space symmetry of the  $\text{TiO}_{0.3}\text{D}_{0.1}$  has been determined among the other space symmetries *e.g.* P31c, P31c and P3m1 which also give no extra Bragg reflection.

The weighted residuals,  $R_w(=[\sum w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2 / \sum w|F_{\text{obs}}|^2]^{1/2})$  for P31m, P31c, P31c and P3m1 became respectively 0.10, 0.22, 0.13 and 0.25 for X-ray diffraction data. Although most possible alternative choice other than the P31m was P31c, the least squares calculation on the neutron diffraction data indicated that the  $R_w$  for the P31c can not be shrunk under 0.198, which is significantly higher than the case of the P31m,  $R_w=0.135$ . The number of adjustable structural parameters *e.g.* positional and thermal parameters and occupation probabilities for the symmetry choices P31m and P31c are both 46. Because of obvious difference in the  $R_w$ s in two cases, the Hamilton's significant test<sup>(24)</sup> may not be needed to choose a suitable space symmetry as the P31m-type. The reason why the space symmetry of

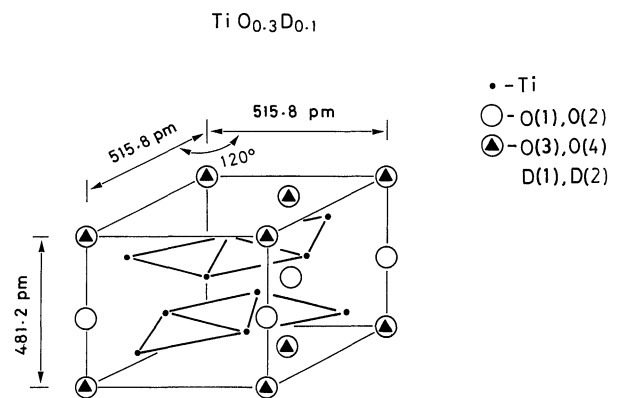


Fig. 5 A unit cell of the trigonal (P31m)  $\text{TiO}_{0.3}\text{D}_{0.1}$ . Deuterium atoms occupy two different octahedral sites where oxygen atoms co-occupy statistically.

the present sample is not identical with that of the  $\alpha''$ - $\text{TiO}_{0.3}$  is not yet clear.

The present study shows that titanium atoms are located at two  $3c(0.340\ 0\ 0.230)$  and  $3c(0.667\ 0\ 0.728)$  sites. It is noted that the interplanar distances between titanium (001) layers equal  $1/2$  of the  $c$ -axis with experimental error of  $\pm 0.002c$ . Oxygen atoms are located at two different  $2b(1/3\ 2/3\ z)$  sites with  $z=0.444$  and  $z=0.0$  and two different  $1a(0\ 0\ z)$  sites with  $z=0.444$  and  $z=0.0$ , respectively. The occupation probabilities at  $2b$ - and  $1a$ -sites with  $z=0.444$  are almost the same level at  $0.42(3)$  and  $0.43(3)$ . In the other  $2b$ - and  $1a$ -sites with  $z=0.0$ , the occupation probabilities are also quite similar,  $0.19(3)$  and  $0.18(7)$ . Deuterium atoms are located at O-sites, that are  $2b$ - and  $1a$ -sites with  $z=0.0$ . It is interesting to point out that combined occupation probabilities of oxygen plus deuterium atoms at O-sites with  $z=0.0$ , being  $0.37(11)$  and  $0.39(5)$  for the  $1a$ - and  $2b$ -sites respectively, are comparable with those at another O-sites with  $z=0.444$  which are only occupied by oxygen atoms. The thermal parameter,  $B=8\pi^2\langle u^2 \rangle$ , of titanium atoms at two  $3c$ -sites are about  $B=14700$  and  $600\ \text{pm}^2$ , respectively. Large difference could be attributed to the static displacements due to short range ordering of oxygen atoms (details will be described elsewhere). The thermal parameter of deuterium atoms is found at the reasonable level of  $B=31600\ \text{pm}^2$  which agrees well with the value discussed in the previous section.

### V. Crystal Structure of $\text{ZrO}_{0.4}\text{D}_{0.1}$

Refined structural parameters of the  $\text{ZrO}_{0.4}\text{D}_{0.1}$  are listed in the second column of Table 2. The space symmetry of the  $\text{ZrO}_{0.4}\text{D}_{0.1}$  is designated as the same type of  $P312(\text{No.}149)$  which was assigned for the  $\alpha''$ - $\text{ZrO}_{0.4}$  by Hashimoto<sup>(18)</sup>. Figure 6 shows an atomic arrangement of the  $\text{ZrO}_{0.412}$  lattice. A rhombic cell drawn with thick lines

corresponds to a unit cell. A projection of the lattice along  $c$ -axis is presented. The lattice constants are  $a=b=561.5\ \text{pm}$   $c=520.4\ \text{pm}$ . Zirconium atoms are located at  $6l(0.3350\ 0.0017\ 0.2486)$  sites corresponding to the every corner of pyramids of which the tetrahedral sites are at the centers in Fig. 6. Open circles are oxygen atoms trapped at octahedral sites,  $(0\ 0\ 0)$ ,  $(2/3\ 1/3\ 1/2)$  and  $(1/3\ 2/3\ 1/2)$ . The former two sites are occupied almost equally, the occupation probabilities being about 0.9. The latter site is occupied with the probability of about 0.7. The radius of the oxygen atoms in the Fig. 6 are drawn according to the occupation probabilities. Present study shows that zirconium and oxygen atoms are located at the same positions as in the  $\alpha''$ - $\text{ZrO}_{0.4}$ <sup>(18)</sup>. The coordinates and the thermal parameters,  $B$ , of zirconium atoms in the  $\text{ZrO}_{0.4}\text{D}_{0.1}$  and the  $\alpha''$ - $\text{ZrO}_{0.4}$  agree well. Figure 7 shows the crystal structure of the  $\text{ZrO}_{0.4}\text{D}_{0.1}$ . Deuterium atoms D(1) and D(2) in the  $\text{ZrO}_{0.4}\text{D}_{0.1}$  are located at  $6l(0.341\ -0.018\ 0.537)$  and  $6l(0.669\ 0.057\ 0.113)$  sites, respectively. Both  $6l$ -sites are T-sites at

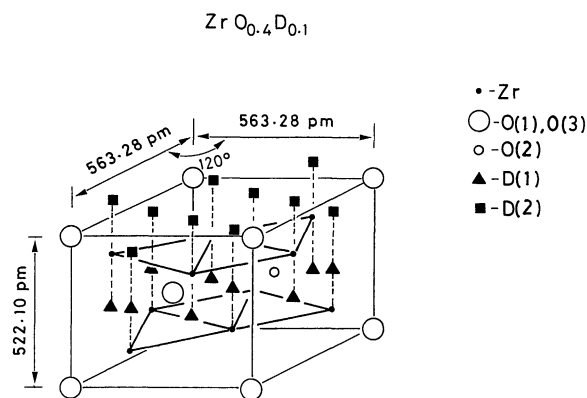


Fig. 7 Structure of the  $\text{ZrO}_{0.4}\text{D}_{0.1}$ . Deuterium atoms are located at  $6l(0.341\ -0.018\ 0.537)$  and  $6l(0.669\ 0.057\ 0.113)$  sites, both of which are T-sites.

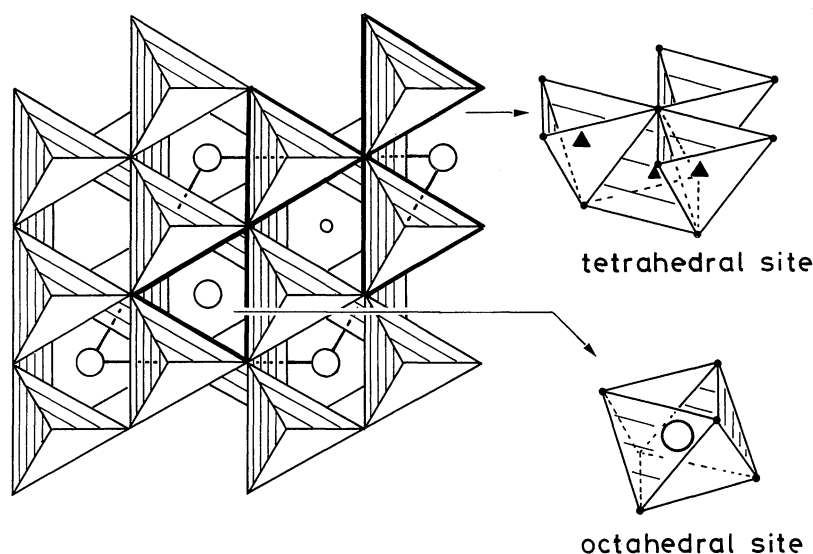


Fig. 6 Schematic presentation of a crystal structure of  $\text{ZrO}_{0.4}$  and interstitial sites. Zirconium atoms, which form a hexagonal close packed lattice, are at the every corner of pyramids. Tetrahedral sites are at the center of pyramids. Vacant circles are oxygen atoms.

which the first nearest atoms are oxygen atoms. Ideal coordinates of T-sites are  $6l(1/3 \ 0 \ 7/12)$  and  $6l(2/3 \ 0 \ 1/12)$ . Experimentally obtained coordinates show some displacements of deuterium atoms along the  $c$ -axis. D(1) atoms move from the ideal position toward oxygen layer appreciably. But the displacement of D(2) atoms is almost negligible. The T-sites, adjacent to the oxygen layer at  $z=0$ , are occupied frequently than the T-site being closer to the oxygen-rich layer at  $z=1/2$ .

The thermal vibration amplitude,  $u_{ij}^2$ , of each atom becomes larger in the directions [100] and [010] than in the [001] direction, but those of oxygen and deuterium atoms are almost isotropic. The thermal parameter of deuterium atoms,  $B=36800 \text{ pm}^2$ , in the  $\text{ZrO}_{0.4}\text{D}_{0.1}$  are about 50% larger than the estimated value,  $B=24100 \text{ pm}^2$ , from the neutron inelastic scattering spectrum reported in section III.

## VI. Discussion

The crystal structure of the  $\text{TiO}_{0.3}\text{D}_{0.1}$  and the  $\text{ZrO}_{0.4}\text{D}_{0.1}$  have almost identical or identical space symmetries of those of the deuterium-free crystals  $\text{TiO}_{0.3}$  and  $\text{ZrO}_{0.4}$ , respectively. Deuterium atoms are trapped at O-sites and T-sites in the  $\text{TiO}_{0.3}\text{D}_{0.1}$  and in the  $\text{ZrO}_{0.4}\text{D}_{0.1}$ , respectively. The latter has a larger unit cell than the other. The shortest interatomic distances between two deuterium atoms, deuterium-metal atoms, deuterium-oxygen atoms and two oxygen atoms in the  $\text{TiO}_{0.3}\text{D}_{0.1}$  and the  $\text{ZrO}_{0.4}\text{D}_{0.1}$  are listed in Table 3. It is interesting to note that the D-D and D-metal distances in the two crystals are similar even though the trapping sites for deuterium atoms are different. On the other hand, the D-O distances i.e. 297.8 pm in the  $\text{TiO}_{0.3}\text{D}_{0.1}$  and 212.8 pm in the  $\text{ZrO}_{0.4}\text{D}_{0.1}$  are different.

In the  $\text{TiO}_{0.3}\text{D}_{0.1}$  crystal, deuterium atoms are trapped at alternative O-site layers which consist of  $1a(0 \ 0 \ 0)$  and  $2b(1/3 \ 2/3 \ 0)$  sites, both occupied by oxygen atoms statistically. The O-site layers, which are  $1a(0 \ 0 \ 0.444)$  and  $2b(1/3 \ 2/3 \ 0.444)$  sites and are highly occupied by oxygen atoms, do not absorb deuterium atoms. On the other hand, deuterium atoms are trapped at every T-sites at  $6l(0.342 \ -0.018 \ 0.537)$  and  $6l(0.559 \ 0.057 \ 0.113)$  in the  $\text{ZrO}_{0.4}\text{D}_{0.1}$  lattice. The site occupation probabilities at two  $6l$ -sites are quite similar, 0.04(1) and 0.06(4), respectively.

Oxygen atoms seem to weakly repel deuterium atoms in the  $\text{TiO}_{0.3}\text{D}_{0.1}$  and the  $\text{ZrO}_{0.4}\text{D}_{0.1}$  lattices, but the repulsive interaction is weak enough to retain the crystal at the semi-original structure.

Table 3 The shortest interatomic distances in the  $\text{ZrO}_{0.4}\text{D}_{0.1}$  and the  $\text{TiO}_{0.3}\text{D}_{0.1}$ .

Specimen	Distance (pm)				
	D-D	D-metal	D-O	O-metal	O-O
$\text{TiO}_{0.3}\text{D}_{0.1}$	297.8	201.4	297.8	201.4	297.8
$\text{ZrO}_{0.4}\text{D}_{0.1}$	270.7	189.7	212.8	228.3	325.2

The unit cell dimensions,  $a=b$  and  $c$  of the  $\text{TiO}_{0.3}\text{D}_{0.1}$  and the  $\text{ZrO}_{0.4}\text{D}_{0.1}$  lattices are  $a=b=515.8 \ c=481.2$  and  $a=b=563.28 \ c=522.10 \text{ pm}$ , respectively. These values are compared with those of the  $\text{TiO}_{0.3}$  at  $a=b=514.1 \ c=476.7 \text{ pm}$  and of the  $\text{ZrO}_{0.4}$  at  $a=b=561.5 \ c=520.4 \text{ pm}$ . The lattice parameters in the Zr-O-D system are expanded almost hydrostatically about 0.3% relative to the deuterium-free lattice but the  $c$ -axis length in the Ti-O-D system expanded about 1% while the  $a$ -axis expanded about 0.3% by the deuterium charging. Nonhydrostatic lattice expansion in the Ti-O-D system may be attributed to the formation of deuterium atom layers perpendicular to the  $c$ -axis.

## VII. Conclusion

The energy eigenvalues of hydrogen local modes in the  $\text{TiO}_{0.3}\text{H}_{0.1}$  are determined to be 11.1 and 8.2 kJ/mol (115 and 85 meV) with the FWHM of 3.1 kJ/mol (32 meV) being correspondent to the experimental error. The former value corresponds to the vertical singlet and the latter corresponds to the horizontal doublet. On the other hand, the energy eigenvalues of the modes in the  $\text{ZrO}_{0.4}\text{H}_{0.1}$  are determined as 12.4 and 13.1 kJ/mol (129 and 136 meV) with the FWHM of 2.1 kJ/mol (20 meV). The two energy eigenvalues are those of the singlet- and the doublet-modes, respectively.

The crystal structures of the  $\text{TiO}_{0.3}\text{D}_{0.1}$  and the  $\text{ZrO}_{0.4}\text{D}_{0.1}$  are determined by means of X-ray and neutron single-crystal diffraction measurements. In the  $\text{TiO}_{0.3}\text{D}_{0.1}$  lattice, deuterium atoms are trapped at O-sites which are statistically co-occupied by oxygen atoms. In the  $\text{ZrO}_{0.4}\text{D}_{0.1}$  lattice, deuterium atoms are located at T-sites in a random manner.

### Acknowledgment

Invaluable discussions by Professor S. Yamaguchi during the present research is thankfully acknowledged. We also thank Mr. K. Nemoto for his technical assistance on the neutron diffraction work in JAERI.

This work has partly been supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

### REFERENCES

- (1) P. P. Narange, G. L. Paul and K. N. R. Taylor: *J. Less-Common Metals*, **56** (1977), 125.
- (2) R. Khoda-Bakhoh and D. K. Ross: *J. Phys. (F) Met. Phys.*, **12** (1982), 15.
- (3) R. Hempelmann, D. Richter and B. Strizker: *J. Phys. (F) Met. Phys.*, **12** (1982), 79.
- (4) S. Mukawa, T. Kajitani and M. Hirabayashi: *J. Less-Common Metals*, **103** (1984), 45.
- (5) S. Yamaguchi: *J. Phys. Soc. Japan*, **27** (1969), 155.
- (6) A. Jostsons and A. E. Jenkins: *Trans. Met. Soc. AIME*, **239** (1967), 1318.
- (7) M. Hirabayashi, S. Yamaguchi, T. Arai, H. Asano and S. Hashimoto: *Phys. Status Solidi*, (a), **23** (1974), 331.
- (8) C. E. Ells and A. D. McQuillan: *J. Inst. Metals*, **85** (1956), 89.
- (9) S. Anderson, B. Collen, U. Kuylenstierna and A. Magneli: *Acta Chem. Scand.*, **11** (1957), 1641; *ibid.*, **11** (1957) 1653.
- (10) R. J. Wasilewski: *Trans. Met. Soc. AIME*, **221** (1961), 1231.

- (11) F. R. L. Schoening and F. Witt: *Acta Crystall.*, **18** (1965), 609.
- (12) A. Jostsons and A. S. Maliu: *ibid.*, **B24** (1968), 211.
- (13) M. Koiwa and M. Hirabayashi: *J. Phys. Soc. Japan*, **27** (1969), 801; *ibid.*, **27** (1969), 807.
- (14) B. Holmbery and T. Dagerhamn: *Acta Chem. Scand.*, **15** (1961), 919.
- (15) S. Yamaguchi: *J. Phys. Soc. Japan*, **24** (1968), 855.
- (16) S. Yamaguchi and M. Hirabayashi: *J. Appl. Cryst.*, **3** (1970), 319.
- (17) M. Hirabayashi, S. Yamaguchi, T. Arai, H. Asano and S. Hashimoto: *J. Phys. Soc. Japan*, **32** (1972), 1157.
- (18) S. Hashimoto, H. Iwasaki, S. Ogawa, S. Yamaguchi and M. Hirabayashi: *J. Appl. Cryst.*, **7** (1974), 67.
- (19) Y. Sugizaki, S. Yamaguchi, S. Hashimoto, M. Hirabayashi and Y. Ishikawa: *J. Phys. Soc. Japan*, **54** (1985), 2543.
- (20) M. Hirabayashi, M. Koiwa and S. Yamaguchi: *The Mechanism of Phase Transformations in Crystalline Solids*, Institute of Metals Monograph and Report Series, No. 33, (1969), p. 207.
- (21) N. Watanabe, M. Furusaka and M. Misawa: *Res. Rep. Lab. Nucl. Sci. Tohoku Univ.*, **12** (1979), 72.
- (22) P. Coppens, T. N. Guru Row, P. Leung, E. D. Stevens, P. J. Becker and Y. W. Yang: *Acta Cryst.*, **A35** (1979), 63.
- (23) T. Kajitani, T. Kawase, K. Yamada and M. Hirabayashi: *Trans. JIM*, **27** (1986), 639.
- (24) W. C. Hamilton: *Acta Crystall.*, **18** (1965), 502.