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# Hydrogen in nonstoichiometric cubic titanium monoxides: X-ray and neutron diffraction, neutron vibrational spectroscopy and NMR studies



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# ABSTRACT

Hydrogen-induced changes in the properties of transition-metal oxides have attracted much recent attention due to numerous applications of these materials including catalysis, H<sub>2</sub> production, low-temperature H<sub>2</sub> sensing, solar cells, and air purification. However, basic properties of hydrogenated titanium monoxides have not been investigated so far. In the present work, we report the results of the first studies of the crystal structure, vibrational spectra, and mobility of H atoms in TiO<sub>0.72</sub>H<sub>0.30</sub> and TiO<sub>0.96</sub>H<sub>0.14</sub> using X-ray diffraction (XRD), neutron powder diffraction, neutron vibrational spectroscopy, and nuclear magnetic resonance (NMR). The hydrogenated compound TiO<sub>0.72</sub>H<sub>0.30</sub> is found to retain the disordered cubic B1-type structure of the initial titanium monoxide, where H atoms exclusively occupy vacancies in the oxygen sublattice. It has been revealed that hydrogenation of the disordered cubic TiO<sub>0.96</sub> leads to the formation of the two-phase compound  $TiO_{0.96}H_{0.14}$ , where the disordered B1-type phase coexists with the monoclinic phase of Ti<sub>5</sub>O<sub>5</sub> type with an ordered arrangement of vacancies. In both phases, H atoms are found to occupy only vacancies in the oxygen sublattice. The low-temperature inelastic neutron scattering spectra of  $TiO_{0.72}H_{0.30}$  and  $TiO_{0.96}H_{0.14}$  in the energy transfer range of 40–180 meV exhibit a single peak due to optical oxygen vibrations (centered on about 60 meV) and a broad structure at 90-170 meV due to optical H vibrations. The unusual width of this structure can be attributed to the broken symmetry of hydrogen sites in the titanium monoxides: because of the presence of vacancies in the titanium sublattice, the actual point symmetry of these sites appears to be lower than octahedral. Proton NMR measurements have revealed that both hydrogenated compounds are metallic; no signs of hydrogen diffusive motion in TiO<sub>0.72</sub>H<sub>0.30</sub> and  $TiO_{0.96}H_{0.14}$  at the frequency scale of about  $10^5 \text{ s}^{-1}$  have been found up to 370 K.

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# 1. Introduction

Hydrogen is considered as a prospective environment-friendly energy carrier for the future economy. Furthermore, hydrogen can be absorbed by various crystalline solids, leading to strong modifications of their properties. Hydrogen-induced changes in the properties of transition-metal oxides have attracted considerable recent attention due to numerous applications of these materials related to catalysis, H<sub>2</sub> production, low-temperature H<sub>2</sub> sensing, solar cells, and

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https://doi.org/10.1016/j.jallcom.2021.161353 0925-8388/© 2021 Elsevier B.V. All rights reserved. air purification [1–5]. In the present work, we address the behavior of hydrogen in cubic titanium monoxides  $TiO_y$  having the *B*1 (NaCltype) structure and the homogeneity range from  $TiO_{0.80}$  to  $TiO_{1.25}$ . These oxides belong to the group of strongly nonstoichiometric compounds  $MX_y$  (where M is a transition metal and X is C, N or O) [6–8]. The unusual structural feature of titanium monoxide is that it has high concentrations of vacancies in both the metal (Ti) and nonmetal (O) sublattices. While in most of the related compounds, deviations from the stoichiometry occur either in a metal sublattice [9–11] or in a non-metal one [12–16], structural vacancies in both the metal and non-metal sublattices simultaneously exist only in  $TiO_y$  [17–19],  $VO_y$  [20,21], and  $NbO_{1.00}$  [22] monoxides. In order to describe the structure of titanium monoxide correctly, its composition should be written as  $\text{Ti}_x O_z \equiv \text{Ti}O_y$  or  $\text{Ti}_x \bullet_{1-x} O_z \bullet_{1-z} \equiv \text{Ti}O_y$ , where y = z/x, and  $\bullet$  and  $\bullet$  are the vacancies in the metal (Ti) and non-metal (O) sublattices, respectively [23,24]. In disordered phases, atoms and vacancies randomly occupy the sites of the corresponding sublattices.

A number of cubic MX<sub>v</sub> compounds can absorb hydrogen from the gas phase forming ternary hydrides MX<sub>v</sub>H<sub>8</sub>. Usually hydrogen atoms occupy the vacant octahedral sites of the non-metal sublattice [25–28]. It should be noted that the volume of these vacant pores considerably exceeds that of the regular interstitial sites in metals. This suggests that H atoms may be displaced from the centers of the octahedral vacancies. In fact, off-center hydrogen sites have been observed in NbC<sub>0.71</sub>H<sub>0.28</sub> [29]. It has also been found that such offcenter location of H atoms in NbC<sub>0.71</sub>H<sub>0.28</sub> is accompanied by enhanced hydrogen mobility [30,31]. To the best of our knowledge, the only work addressing hydrogen absorption in cubic titanium monoxides was published by Pavlov et al. [32]. However, basic features of the behavior of hydrogen and its ability to compensate native defects in titanium monoxides have not been investigated so far. In particular, there is no direct information on the positions and mobility of H atoms in these compounds. The aims of the present work are to study the positions and mobility of H atoms and the vibrational spectra in hydrogenated cubic titanium monoxides by means of Xray diffraction (XRD), neutron diffraction, neutron vibrational spectroscopy, and nuclear magnetic resonance (NMR).

# 2. Experimental details

The samples of nonstoichiometric cubic titanium monoxide with different oxygen content were synthesized by solid-state sintering of mixed powders of metallic Ti and titanium dioxide  $TiO_2$ . The synthesis was performed in vacuum (at a pressure of  $1.3 \times 10^{-3}$  Pa) at 1770 K for 70 h, with an additional grinding of the samples after each 20 h. To obtain a disordered state of titanium monoxides after the synthesis, the samples were further annealed in quartz ampoules under vacuum at 1330 K for 3 h and quenched into water; the estimated quenching speed was about 200 K/s [33]. The details of the synthesis of titanium monoxides were reported earlier [34].

The titanium and oxygen contents were determined by the increase in mass after oxidation of the  $TiO_{\nu}$  powders up to  $TiO_2$ . The oxidation was made in air following the heating of the powders up to 1200 K for 5-8 h, until the sample reached a constant mass. The increase in mass was measured by thermogravimetric analysis using the Q-1500D derivatograph. To determine vacancy concentrations in the metal and non-metal sublattices of the titanium monoxide, we have performed pycnometric measurements of the density d of the quenched disordered samples. The measurements were made on carefully grinded powders with the average particle size of 3-5 µm using pycnometers with the volume of 1 cm<sup>3</sup> at the stabilized temperature of 298 K; high-purity kerosene was used as a working liquid. The fraction x of filled Ti sites in the metal sublattice of disordered titanium monoxide  $Ti_xO_z$  was determined as [34]  $x = da^3C_{Ti}/da^3$  $Nm_uA_{Ti}$ , where *a* is the lattice constant, N = 4 is the number of chemical formula units of TiO<sub>y</sub> in the elementary cell,  $m_{\rm u}$  = 1.66 × 10<sup>-24</sup> g is the atomic mass unit,  $A_{Ti}$  is the atomic weight of Ti, and  $C_{Ti}$  is the mass fraction of Ti in monoxide. The fraction z of filled O sites in the non-metal sublattice was determined as z = xy. The accuracy of the site fraction determination was ±0.02.

Powdered samples of disordered cubic titanium monoxide were charged with hydrogen at a pressure of about 1 bar using a Sieverts-type vacuum system. After heating the monoxide in vacuum up to 973 K,  $H_2$  gas was admitted into the system at this temperature. The amount of absorbed hydrogen was determined from the pressure change in the calibrated volume of the system after slowly cooling down to room temperature. Two hydrogenated samples,  $TiO_{0.72}H_{0.30}$ 

and  $TiO_{0.96}H_{0.14}$ , were chosen for detailed studies of the structure and H dynamics.

XRD measurements were performed on the Shimadzu [35] XRD-7000 diffractometer using Cu  $K_{\alpha 1,2}$  radiation in the scattering angle  $(2\theta)$  range from 10 to  $157^{\circ}$  with a step of  $0.02^{\circ}$ . Profile refinements of the XRD patterns were made using the X'Pert Plus program package [36]. All neutron scattering measurements were undertaken at the NIST Center for Neutron Research (Gaithersburg, Maryland, USA). Neutron diffraction measurements were performed on the high-resolution powder diffractometer BT1 [37] using the Cu (311) monochromator, which provided an incident neutron wavelength  $\lambda$  of 1.5402 Å. Neutron diffraction patterns were recorded in the scattering angle range  $5^{\circ} \le 2\theta \le 162^{\circ}$  with a step of 0.05°. Profile refinements of the diffraction patterns were made by Rietveld analysis using the GSAS code as implemented in EXPGUI [38,39]. Inelastic neutron scattering (INS) measurements of the vibrational spectra at 4 K were performed on the filter-analyzer neutron spectrometer (FANS) [40]. Typical ranges of the neutron energy loss  $\hbar\omega$  measured on FANS were 40-180 meV, with an energy resolution of about 4-5% of  $\hbar\omega$ . Vertical error bars associated with all INS spectra in this paper correspond to one standard deviation. After completing the neutron scattering experiments on  $TiO_{0.72}H_{0.30}$  and  $TiO_{0.96}H_{0.14}$ , hydrogen was removed from these samples by annealing in vacuum at 1073 K, and the room-temperature neutron diffraction measurements and INS measurements at 4 K were repeated on the dehydrogenated samples.

Measurements of the proton NMR spectra and spin-lattice relaxation rates were performed on a pulse spectrometer with guadrature phase detection at the frequencies  $\omega/2\pi = 14, 23.8$ , and 90 MHz. The magnetic field was provided by a 2.1 T iron-core Bruker magnet. A home-built multinuclear continuous-wave NMR magnetometer working in the range 0.32-2.15 T was used for field stabilization. For rf pulse generation, we used a home-built computer-controlled pulse programmer, the PTS frequency synthesizer (Programmed Test Sources, Inc.), and a 1 kW Kalmus wideband pulse amplifier. Typical values of the  $\pi/2$  pulse length were 2–3  $\mu$ s. A probe head with the sample was placed into an Oxford Instruments CF1200 continuous-flow cryostat using helium or nitrogen as a cooling agent. The sample temperature, monitored by a chromel-(Au-Fe) thermocouple, was stable to ±0.1 K. Nuclear spin-lattice relaxation rates were measured using the saturation - recovery method; typical errors in the measured relaxation rates were about 5%. NMR spectra were recorded by Fourier transforming the solid echo signals.

# 3. Results and discussion

# 3.1. XRD and neutron diffraction

The room-temperature XRD patterns of the initial monoxides  $TiO_{0.72}$  (actual composition  $Ti_{0.95}\bullet_{0.05}O_{0.69}\bullet_{0.31}$ ) and  $TiO_{0.96}$  (actual composition  $Ti_{0.89}\bullet_{0.11}O_{0.85}\bullet_{0.05}$ ) are shown in Figs. 1a and 2a, respectively. Both oxides are found to be single-phase compounds having the disordered cubic *B*1-type structure (space group  $Fm\bar{3}m$ ) with vacancies in titanium and oxygen sublattices and the lattice constants  $a_{B1} = 4.1934$  Å ( $TiO_{0.72}$ ) and 4.1827 Å ( $TiO_{0.96}$ ). The accuracy of the lattice constant determination was ±0.0002 Å.

The room-temperature XRD and neutron diffraction patterns of the hydrogenated TiO<sub>0.72</sub>H<sub>0.30</sub> are shown in Fig. 1a and b. This hydrogenated compound retains the disordered cubic *B*1-type structure, and its lattice parameter  $a_{B1}$  (4.2076 Å and 4.2057 Å from XRD and neutron diffraction, respectively) is higher than that of the starting oxide TiO<sub>0.72</sub>. Thus, the absorption of hydrogen leads to a considerable increase in the unit cell volume of a cubic titanium monoxide.



**Fig. 1.** (a) Experimental ( $\times$ ) and calculated (red line) XRD patterns for the starting cubic monoxide TiO<sub>0.72</sub>; experimental (+) and calculated (black line) XRD patterns for the hydrogenated TiO<sub>0.72</sub>H<sub>0.30</sub>. Vertical bars indicate the calculated positions of Bragg peaks for the disordered cubic *B*1-type phase of TiO<sub>0.72</sub>H<sub>0.30</sub>. The line in the lower part of the figure shows the difference between the observed and calculated XRD patterns for TiO<sub>0.72</sub>H<sub>0.30</sub>. (b) Experimental (circles), calculated (red line) and difference (black line in the lower part of the figure) neutron powder diffraction profiles for TiO<sub>0.72</sub>H<sub>0.30</sub>. Vertical bars indicate the calculated positions of Bragg peaks.

It is interesting to note that, in contrast to the XRD pattern, the Bragg peaks with even Miller indices (200), (220), (222), (400), (420), (422), and (400) in the neutron diffraction pattern of TiO<sub>0.72</sub>H<sub>0.30</sub> are extremely weak. This is related to the specific combination of neutron scattering lengths for the nuclei forming the hydrogenated titanium oxide. In fact, the coherent neutron scattering lengths for Ti, O, and H are  $-3.348 \times 10^{-15}$  m,  $5.803 \times 10^{-15}$  m, and  $-3.742 \times 10^{-15}$  m, respectively [41]. Since the sign of the coherent scattering length for O is opposite to those for Ti and H, the corresponding contributions to the structure factors for the Bragg peaks with even Miller indices tend to compensate each other. For positions of H atoms in  $TiO_{0.72}H_{0.30}$ , we have considered two possibilities: the centers of oxygen vacancies (4b (1/2, 1/2, 1/2)) sites which can be treated as the octahedral interstitials in the Ti sublattice) and the tetrahedral interstitials in the Ti sublattice (8c (1/4, 1/4, 1/4))sites); see Fig. 3.

The refinement of the neutron diffraction data for  $TiO_{0.72}H_{0.30}$  has shown that any attempts to put a fraction of H atoms in 8c sites worsen the agreement between the model and the experimental diffraction patterns. Thus, for the final refinement, the model with H



**Fig. 2.** (a) Experimental  $(\times)$  and calculated (red line) XRD patterns for the starting cubic monoxide TiO<sub>0.96</sub>; experimental (+) and calculated (black line) XRD patterns for the hydrogenated TiO<sub>0.96</sub>H<sub>0.14</sub>. Long and short vertical bars indicate, respectively, the calculated positions of Bragg peaks for the disordered cubic *B*1-type phase and the ordered monoclinic Ti<sub>5</sub>O<sub>5</sub> type phase of the hydrogenated compound. The line in the lower part of the figure shows the difference between the observed and calculated XRD patterns for TiO<sub>0.96</sub>H<sub>0.14</sub>. (b) Experimental (circles), calculated (red line), and difference (black line in the lower part of the figure) neutron powder diffraction profiles for TiO<sub>0.96</sub>H<sub>0.14</sub>. Vertical bars indicate the calculated positions of Bragg peaks for the cubic (top) and monoclinic (bottom) phases.

atoms occupying only 4*b* sites has been used. The results of this refinement are shown in Table 1, and the corresponding fit of the neutron diffraction pattern is presented in Fig. 1b. It should be noted that the occupancies of Ti and O sublattices resulting from the refinement of the neutron diffraction data for  $TiO_{0.72}H_{0.30}$  are close to the corresponding values determined by other methods. The total hydrogen content in this compound derived from the neutron diffraction data is also consistent both with the vacancy concentration in the oxygen sublattice and with H concentration obtained from the absorption.

Hydrogenation of TiO<sub>0.96</sub> leads to the formation of TiO<sub>0.96</sub>H<sub>0.14</sub>, where in addition to the main cubic *B*1-type phase, a second low-symmetry phase appears. Analysis of the XRD pattern (Fig. 2a) has shown that this minor phase is the monoclinic phase (space group C2/m) of Ti<sub>5</sub>O<sub>5</sub> (Ti<sub>5</sub>=1O<sub>5</sub>D<sub>1</sub>) type with an ordered arrangement of vacancies [24,42,43]. This ordered phase is known to exist at  $T \le 1300$  K for titanium monoxides in the homogeneity range from TiO<sub>0.9</sub> to TiO<sub>1.1</sub> [29,44,45]. Our starting nearly stoichiometric



**Fig. 3.** Elementary cell of the disordered nonstoichiometric cubic titanium monoxide (space group  $Fm\bar{3}m$ ). Blue circles: 4(a) sites randomly occupied by Ti atoms; open circles: 4(b) sites randomly occupied by O atoms (octahedral interstitial sites of the Ti sublattice); red crosses: 8(c) sites (centers of tetrahedral interstitial sites in the Ti or O sublattices).

#### Table 1

Structural parameters resulting from room-temperature NPD profile refinements for the cubic compound  $TiO_{0.72}H_{0.30}$  with *B*1-type structure (space group  $Fm\overline{3}m$ ,  $a_{B1} = 4.2057(2)$  Å).

Atom	Position	Coordinates			Occupancy	$U_{iso}$ (Å <sup>2</sup> )
		x	у	z		
Ti	4a	0	0	0	0.95(7)	0.002(3)
0	4b	1/2	1/2	1/2	0.70(8)	0.017(4)
Н	4b	1/2	1/2	1/2	0.30(9)	0.10 <sup>a</sup>

Rietveld agreement factors:  $\chi^2 = 1.113$ ,  $R_p = 0.0484$ ,  $R_{wp} = 0.0609$ ,  $R_{F2} = :0.0490$ .

<sup>a</sup> The thermal factor of H is strongly correlated with its occupancy. Refining them simultaneously would not lead to a convergency. Therefore, only the occupancy of H is refined after its thermal factor was refined and then fixed.

monoxide TiO<sub>0.96</sub> has been obtained by quenching (see Section 2) which stabilizes the disordered *B*1-type phase. However, hydrogenation at 973 K appears to facilitate the formation of an ordered phase. The appearance of an ordered phase due to hydrogenation of the nearly stoichiometric cubic titanium monoxide was observed earlier [32]. Similar examples of hydrogen-assisted vacancy ordering have been reported for cubic transition-metal carbides [26,29]. The fractions of the cubic and monoclinic phases determined from the analysis of the XRD pattern for TiO<sub>0.96</sub>H<sub>0.14</sub> are 86 ± 2 wt% and 14 ± 2 wt%, respectively. The neutron diffraction pattern for TiO<sub>0.96</sub>H<sub>0.14</sub> is shown in Fig. 2b. As in the case of TiO<sub>0.72</sub>H<sub>0.30</sub>, for the cubic *B*1-type phase of TiO<sub>0.96</sub>H<sub>0.14</sub>, the Bragg peaks corresponding to even Miller indices are extremely small. The results of the refinement of the neutron diffraction pattern is presented in Fig. 2b.

It should be noted that the lattice parameter of the B1-type phase of the hydrogenated compound appears to be very close to that of the starting monoxide TiO<sub>0.96</sub>. For both coexisting phases, H atoms are found to occupy only the vacant sites of the oxygen sublattice

#### Table 2

Structural parameters resulting from room-temperature NPD profile refinements for the two-phase compound  $TiO_{0.96}H_{0.14}$  containing the disordered cubic phase with B1-type structure and the ordered monoclinic phase of  $Ti_5O_5$  type.

Cubic (space group $Fm\overline{3}m$ ) Ti <sub>0.87</sub> O <sub>0.81</sub> H <sub>0.09</sub> phase with B1-type structure: $a_{B1} = 4.1844$ (1) Å						
Atom	Position	Coordinates		Occupancy	$U_{iso}$ (Å <sup>2</sup> )	

					1 5	150 ( )	
		x	у	z			
Ti	4a	0	0	0	0.870 <sup>e</sup>	0.0110(7)	
0	4b	1/2	1/2	1/2	0.810	0.0046(4)	
Н	4b	1/2	1/2	1/2	0.09(5)	0.32ª	

Monoclinic (space group C2/m) Ti<sub>5,31</sub>O<sub>5,30</sub>H<sub>0.5</sub> phase with the structure of Ti<sub>5</sub>O<sub>5</sub> type:  $a_m = 9.355(1)$  Å,  $b_m = 4.1513(4)$  Å,  $c_m = 5.8765(6)$  Å,  $\beta = 107.70(1)^{\circ}$ 

	_	x	у	Ζ	Occupancy	$U_{iso}(\text{\AA}^2)$
Ti1 <sup>D</sup>	2a	0	0	0	0.31(5)	$0.002(1)^{c}$
Ti 2	2 <i>c</i>	0	0	1/2	1.0	0.002(1)
Ti3 <sup>d</sup>	4i	0.344	0	0.170	1.0	0.002(1)
Ti4 <sup>d</sup>	4i	0.358	0	0.675	1.0	0.002(1)
01 <sup>b</sup>	2d	1/2	0	1/2	0.30(5)	0.0079(8)
H1 <sup>b</sup>	2d	1/2	0	1/2	0.5(1)	0.11 <sup>a</sup>
02	2 <i>b</i>	0	1/	0	1.0	0.0079(8)
			2			
03 <sup>d</sup>	4i	0.1700	0	0.342	1.0	0.0079(8)
04 <sup>d</sup>	4 <i>i</i>	0.1712	0	0.834	1.0	0.0079(8)

Rietveld agreement factors:  $\chi^2 = 0.8767$ ,  $R_p = 0.0470$ ,  $R_{wp} = 0.0579$ ,  $R_{F2} = 0.0868$ .

<sup>a</sup> The thermal factor of H is strongly correlated with its occupancy. Therefore, only the occupancy of H is refined after its thermal factor was refined and then fixed.

 $^{\rm b}$  Vacant sites in the titanium and oxygen sublattices for the ideally ordered  $\rm Ti_5O_5$  structure.

<sup>c</sup> The thermal factors  $U_{iso}$  of the same type atoms were constrained as the same. <sup>d</sup> The atomic position of Ti and O (4*i* sites) were not refined due to the inadequate number of observations. They were fixed as the refined values in the dehydrogenated sample (see Table S2 of the Supplementary Information).

<sup>e</sup> The occupancy and thermal factors of Ti and O in the B1 phase are strongly correlated, thus they cannot be refined simultaneously. The atomic occupancies and thermal factors of Ti and O in Table 2 were refined separately. Different trials of refinement, e.g., fixing the occupancies of Ti and O as the values obtained from XRD and refining thermal factors only, have been done to obtain the best estimation of both the site occupancies and the thermal factors. The R-factors of these refinements do not show significant difference, and the compositions determined in all refinement trials are within the standard error range. Table 2 shows the results of the refinement, where Ti/O occupancies were refined first, followed by the refinement of the thermal factors with the occupancies fixed as the just-refined values.

(which can be considered as octahedral interstitial sites of the titanium sublattice).

The results of room-temperature neutron diffraction measurements for the dehydrogenated samples are presented in the Supplementary Information. The dehydrogenation of  $TiO_{0.72}H_{0.30}$  leads to the formation of disordered cubic *B*1-type monoxide with nearly the same lattice parameter as that for the starting compound  $TiO_{0.72}$ . On the other hand, the dehydrogenation of  $TiO_{0.96}H_{0.14}$  retains the two-phase state of the hydrogenated compound with the coexisting disordered cubic *B*1-type and ordered monoclinic  $Ti_5O_5$ -type phases. This means that the formation of the ordered monoclinic phase is irreversible.

#### 3.2. Neutron vibrational spectroscopy

For metal – hydrogen systems, INS spectra in the energy transfer range of 50–160 meV are usually dominated by the fundamental modes of H optical vibrations. The simplest description of these vibrations is based on the model of a three-dimensional Einstein oscillator [46,47]. For the cubic point symmetry of H sites, this model predicts a single peak in an INS spectrum in the  $\hbar\omega$  range of the fundamental modes. For lower point symmetries of H sites, this peak should be split into two or three peaks.

The experimental low-temperature INS spectra for  $TiO_{0.72}H_{0.30}$  and  $TiO_{0.96}H_{0.14}$  are shown in Figs. 4 and 5. For both compounds, the peak centered at about 60 meV is somewhat separated from the



Fig. 4. The low-temperature inelastic neutron scattering spectrum for TiO<sub>0.72</sub>H<sub>0.30</sub>.

broader part of the spectrum at higher energy transfers. This lowenergy peak can be ascribed to optical vibrations of oxygen atoms. Indeed, additional INS measurements on the dehydrogenated titanium monoxide samples have shown that the shape and the position of this peak remain nearly unchanged after removing hydrogen (see Figs. S3 and S4 of the Supplementary Information). It is interesting to note that a similar low-energy peak centered at about 78 meV and attributed to optical vibrations of carbon atoms was also observed in the related carbide system NbC<sub>1-y</sub>H<sub>x</sub> [29]. The shift of the low-energy peak from 78 meV (for the carbide system) to 60 meV (for the oxide system) is qualitatively consistent with the heavier oscillating mass of O compared to that of C.

The high-energy part of INS spectra (between ~90 meV and 170 meV) for  $TiO_{0.72}H_{0.30}$  and  $TiO_{0.96}H_{0.14}$  should be attributed to H

vibrations in the oxygen vacancies of titanium monoxides. In terms of the Einstein model for local vibrations, for H atoms occupying the centers of octahedral vacancies, one may expect a single nearly-symmetric peak in the vibrational spectrum. However, the observed high-energy part of the vibrational spectra is very broad and asymmetric (Fig. 4 and 5). Indeed, the spectra look like superpositions of two broad bands centered at about 115 meV and about 155 meV. For  $TiO_{0.96}H_{0.14}$  containing the ordered monoclinic phase, the high-energy band at about 155 meV appears to be the dominant one; therefore, this band may be ascribed to the characteristic environment of H in the monoclinic phase. It should be noted that the volume of the voids formed by oxygen vacancies is too large for H atoms, so that a hydrogen atom can be easily displaced from the geometrical center of the vacancy. Such displacements were



Fig. 5. The low-temperature inelastic neutron scattering spectrum for TiO<sub>0.96</sub>H<sub>0.14</sub>.



Fig. 6. Temperature dependence of the proton spin-lattice relaxation rates measured at 14, 23.8, and 90 MHz for TiO<sub>0.72</sub>H<sub>0.30</sub>.

previously observed for the related NbC<sub>1-y</sub>H<sub>x</sub> system [29]. Another factor breaking the ideal point symmetry of H sites in TiO<sub>y</sub> is the presence of vacancies in the *titanium* sublattice. This means that, for a considerable number of H atoms, the nearest-neighbor environment is no longer octahedral. In contrast to the case of Ti monoxides, cubic Nb carbides contain vacancies only in the carbon sublattice; because of this feature, the vibrational spectrum of H in Ti monoxides appears to be much broader than that in NbC<sub>1-y</sub>H<sub>x</sub> [29]. In this respect, the vibrational neutron spectroscopy proves to be a sensitive probe of the local structure.

# 3.3. Nuclear magnetic resonance

The temperature dependences of the proton spin-lattice relaxation rates  $R_1$  measured at different resonance frequencies for TiO<sub>0.72</sub>H<sub>0.30</sub> and TiO<sub>0.96</sub>H<sub>0.14</sub> are shown in Figs. 6 and 7. As can be seen from these figures, for both samples at T < 200 K, the relaxation rate increases nearly linearly with temperature, being frequencyindependent. Such a behavior is typical of the  $R_1$  contribution due to the interaction between nuclear spins and conduction electrons (Korringa contribution) [48]. Therefore, we can conclude that both



Fig. 7. Temperature dependence of the proton spin-lattice relaxation rates measured at 23.8 and 90 MHz for TiO<sub>0.96</sub>H<sub>0.14</sub>.

samples are metallic. For the Korringa contribution, the value of  $C_e = R_1/T$  is proportional to the square of the density of electron states at the Fermi level [48]. The values of  $C_e$  determined from our experimental data at T < 200 K are  $6.7 \times 10^{-3} \text{ s}^{-1} \text{ K}^{-1}$  and  $5.3 \times 10^{-3} \text{ s}^{-1} \text{ K}^{-1}$  for TiO<sub>0.72</sub>H<sub>0.30</sub> and TiO<sub>0.96</sub>H<sub>0.14</sub>, respectively. The observed deviation from the linear temperature dependence of  $R_1$  for TiO<sub>0.96</sub>H<sub>0.14</sub> at T > 250 K (see Fig. 7) can be attributed to a rapid variation of the density of electron states N(E) near the Fermi level  $E_F$  [49]. The absence of any pronounced frequency dependence of the measured  $R_1$  for both hydrogenated samples up to 370 K indicates that, in the studied temperature range, hydrogen diffusion remains too slow to contribute significantly to the proton relaxation rate.

More precisely, the H jump rate in both samples does not exceed  $\sim 10^5$  s<sup>-1</sup> up to 370 K. This is supported by the behavior of the <sup>1</sup>H NMR line widths. The measured proton NMR line widths (full widths at half-maximum) at 80 K are 21 kHz for TiO<sub>0.72</sub>H<sub>0.30</sub> and 10 kHz for TiO<sub>0.96</sub>H<sub>0.14</sub>. Such values are typical of the 'rigid-lattice' proton line widths in metal - hydrogen systems with low H concentrations; they are dominated by static <sup>1</sup>H – <sup>1</sup>H dipole-dipole interactions. The line widths are found to change only slightly over the entire temperature range studied; this means that the dipole-dipole interactions are not averaged by H jump motion. Thus, H atoms in titanium monoxides appear to be immobile on the NMR frequency scale up to 370 K. It should be noted that low diffusive mobility of hydrogen in titanium monoxides is consistent with the exclusive occupancy of the oxygen vacancies by H atoms, since the distance between the centers of the nearest-neighbor oxygen vacancies is rather large (~3 Å).

# 4. Conclusions

In order to clarify basic features of the behavior of hydrogen in titanium monoxides, we have hydrogenated two representative  $TiO_y$  compounds: the substoichiometric  $TiO_{0.72}$  and the nearly stoichiometric  $TiO_{0.96}$ . Our XRD and neutron diffraction data have revealed that hydrogen-induced changes in the crystal structure depend on the concentration of structural vacancies in  $TiO_y$ . While the hydrogenation of  $TiO_{0.72}$  retains the disordered cubic *B*1-type structure of the starting titanium monoxide, the hydrogenation of  $TiO_{0.96}$  leads to the formation of the ordered monoclinic phase of  $Ti_5O_5$  type (space group *C2/m*), in addition to the disordered *B*1-type phase. Although in titanium monoxides, structural vacancies are present in both Ti and O sublattices simultaneously, H atoms are found to occupy only vacancies in the oxygen sublattice (octahedral interstitials in the Ti sublattice).

The low-temperature inelastic neutron scattering spectra of  $TiO_{0.72}H_{0.30}$  and  $TiO_{0.96}H_{0.14}$  in the energy transfer range of 40–180 meV exhibit a single peak due to optical oxygen vibrations (centered at ~60 meV) and a broad structure at 90–170 meV related to optical H vibrations. The unusual width of this structure can be attributed to the broken symmetry of hydrogen sites in the titanium monoxides: because of the presence of vacancies in the titanium sublattice, the actual point symmetry of these sites appears to be lower than octahedral.

Proton NMR measurements have not revealed any signs of hydrogen diffusive motion in  $TiO_{0.72}H_{0.30}$  and  $TiO_{0.96}H_{0.14}$  at the frequency scale of  $\sim 10^5 \text{ s}^{-1}$  up to 370 K. The low diffusive mobility of hydrogen in titanium monoxides is consistent with the structure of these compounds. The Korringa-like behavior of the proton spinlattice relaxation rates at low temperatures indicates that both the studied hydrogenated monoxides are metallic.

The results obtained in this work contribute to understanding the behavior of hydrogen in transition-metal oxides and hydrogen-induced changes in the properties of these compounds. In order to verify, whether these results are common for a broader range of materials, it would be interesting to study the positions and mobility of H atoms in other  $MX_y$  compounds, especially in those having structural vacancies in both the metal and non-metal sublattices. Such studies are planned for the near future.

# **CRediT** authorship contribution statement

A.V. Skripov: Supervision, Writing – original draft. A.V. Soloninin: Investigation, Validation. A.A. Valeeva: Investigation, Visualization. A.I. Gusev: Investigation, Methodology. A.A. Rempel: Methodology, Writing – review & editing. H. Wu: Investigation, Formal Analysis. T.J. Udovic: Investigation, Methodology, Writing – review & editing.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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# Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2021.161353.

# References

- O.K. Varghese, D. Gong, M. Paulose, K.G. Ong, E.C. Dickey, C.A. Grimes, Extreme changes in the electrical resistence of titania nanotubes with hydrogen exposure, Adv. Mater. 15 (2003) 624–627.
- [2] W.P. Chen, K.F. He, Y. Wang, H.L.W. Chan, Z. Yan, Highly mobile and reactive state of hydrogen in metal oxide semiconductors at room temperature, Sci. Rep. 3 (2013) 03149.
- [3] R. Singh, S. Dutta, A review on H<sub>2</sub> production through photocatalytic reactions using TiO<sub>2</sub>/TiO<sub>2</sub>-assisted catalysts, Fuel 220 (2018) 607–620.
- [4] N. Rahimi, R.A. Pax, E.M. Gray, Mechanism of hydrogen modification of titaniumdioxide, J. Alloy. Compd. 815 (2020) 152249.
- [5] J.-P. Jeon, D.H. Kweon, B.J. Jang, M.J. Ju, J.-B. Baek, Enhancing the photocatalytic activity of TiO<sub>2</sub> catalysts, Adv. Sustain. Syst. 4 (2020) 2000197.
- [6] A.A. Valeeva, A.A. Rempel, S.V. Rempel, S.I. Sadovnikov, A.I. Gusev, Nonstoichiometry, structure and properties of nanocrystalline oxides, carbides and sulfides, Russ. Chem. Rev. 90 (2021) 601–626.
- [7] A.A. Rempel, A.A. Valeeva, Thermodynamics of atomic ordering in nonstoichiometric transition metal monoxides, Mendeleev Commun. 20 (2010) 101–103.
- [8] T.T.N. Nguyen, Y.H. Chen, J.L. He, Preparation of inkjet-printed titanium monoxide as p-type absorber layer for photovoltaic purposes, Thin Solid Films 572 (2014) 8–14.
- [9] S.I. Sadovnikov, E.A. Kozlova, E.Yu Gerasimov, A.A. Rempel, A.I. Gusev, Enhanced photocatalytic hydrogen evolution from aqueous solutions on Ag<sub>2</sub>S/Ag heteronanostructure, Int. J. Hydrog. Energy 42 (2017) 25258–25266.
- [10] S.V. Rempel, Y.V. Kuznetsova, A.A. Rempel, Self-assembly of Ag<sub>2</sub>S colloidal nanoparticles stabilized by MPS in water solution, ACS Omega 5 (2020) 16826–16832.
- [11] V. Vallet, C. Carel, Contribution to the study of solid non-stoichiometric iron monoxide. T-P-X diagram, Mater. Res. Bull. 14 (1979) 1181–1194.
- [12] M.I. Chebanenko, D.P. Danilovich, A.A. Lobinsky, V.I. Popkov, A.A. Rempel, A.A. Valeeva, Novel high stable electrocatalyst based on non-stoichiometric nanocrystalline niobium carbide toward effective hydrogen evolution, Int. J. Hydrog. Energy 46 (2021) 16907–16916.
- [13] A.A. Valeeva, A.I. Gusev, Effect of nonstoichiometry on elastic properties of niobium carbide NbC, Int. J. Refract. Met. Hard Mater. 95 (2021) 105435.
- [14] A.A. Valeeva, I.B. Dorosheva, E.A. Kozlova, A.A. Sushnikova, A.Yu Kurenkova, A.A. Saraev, H. Schroettner, A.A. Rempel, Solar photocatalysts based on titanium dioxide nanotubes for hydrogen evolution from aqueous solutions of ethanol, Int. J. Hydrog. Energy 46 (2021) 16917–16924.
  [15] C.J. Smith, C.R. Weinberger, G.B. Thompson, Phase stability and microstructural
- [15] C.J. Smith, C.R. Weinberger, G.B. Thompson, Phase stability and microstructural formations in the niobium carbides, J. Eur. Ceram. Soc. 38 (2018) 4850–4866.

- [16] M.G. Kostenko, A.V. Lukoyanov, A.A. Valeeva, Vacancy ordered structure in nonstoichiometric niobium carbide NbC<sub>0.83</sub>, Mendeleev Commun. 29 (2019) 707–709.
- [17] S.P. Denker, Relation of bonding and electronic band structure to the creation of lattice vacancies in TiO, J. Phys. Chem. Solids 25 (1964) 1397–1405.
- [18] A.A. Valeeva, A.A. Rempel, M.A. Müller, K.J. Reichle, G. Tang, W. Sprengel, H.-E. Schaefer, Identification of atomic vacancies in titanium monoxide by electron microdiffraction and positron annihilation, Phys. Stat. Solidi B 224 (2001) R1–R3.
- [19] I.S. Popov, A.N. Enyashin, A.A. Rempel, Size dependent content of structural vacancies within TiO nanoparticles: quantum-chemical DFTB study, Superlattices Microstruct. 113 (2018) 459–465.
- [20] A.I. Gusev, D.A. Davydov, A.A. Valeeva, Vacancy distribution in nonstoichiometric vanadium monoxide, J. Alloy. Compd. 509 (2011) 1364–1372.
- [21] M.D. Banus, T.B. Reed, A.J. Strauss, Electrical and magnetic properties of TiO and VO, Phys. Rev. B 5 (1972) 2775–2784.
- [22] A.I. Gusev, Niobium monoxide superstructures, JETP Lett. 111 (2020) 176-182.
- [23] J. Ding, T. Ye, H. Zhang, X. Yang, H. Zeng, C. Zhang, X. Wang, Pressure-induced structural phase transition and vacancy filling in titanium monoxide TiO up to 50 GPa, Appl. Phys. Lett. 115 (2019) 101902.
- [24] M.G. Kostenko, A.A. Valeeva, A.A. Rempel, Octahedral clusters in various phases of nonstoichiometric titanium monoxide, Mendeleev Commun. 22 (2012) 245–247.
- [25] K. Yvon, H. Nowotny, R. Kieffer, Zur Kristallstruktur der Carbohydride von Übergangsmetallen, Monatsh. Chem. 98 (1967) 2164–2172.
- [26] V.T. Em, I. Karimov, V.F. Petrunin, I.S. Latergaus, M.M. Antonova, I.I. Timofeyeva, V. Ya. Naumenko, Neutronographic study of cubic titanium carbohydrides, Fiz. Met. Metalloved. 39 (6) (1975) 1286–1289.
- [27] S. Rundqvist, R. Tellgren, Y. Andersson, Hydrogen and deuterium in transition metal – p element compounds: crystal chemical aspects of interstitial solid solubility and hydride phase formation, J. Less Common Met 101 (1984) 145–168.
- [28] G. Renaudin, K. Yvon, S.K. Dolukhanyan, N.N. Aghajanyan, V.S. Shekhtman, Crystal structures and thermal properties of titanium carbo-deuterides as prepared by combustion synthesis, J. Alloy. Compd. 356–357 (2003) 120–127.
- [29] A.V. Skripov, H. Wu, T.J. Udović, Q. Huang, R. Hempelmann, A.V. Soloninin, A.A. Rempel, A.I. Gusev, Hydrogen in nonstoichiometric cubic niobium carbides: neutron vibrational spectroscopy and neutron diffraction studies, J. Alloy. Compd. 478 (2009) 68–74.
- [30] A.V. Soloninin, A.V. Skripov, A.P. Stepanov, V.N. Kozhanov, A.A. Rempel, A.I. Gusev, Spin-lattice relaxation of <sup>13</sup>C and <sup>1</sup>H in hydrogenated niobium and titanium carbides, Phys. Met. Metallogr. 94 (2002) 40–46.
- [31] A.V. Skripov, T.J. Udovic, J.C. Cook, R. Hempelmann, A.A. Rempel, A.I. Gusev, Quasielastic neutron scattering study of hydrogen motion in NbC<sub>0.71</sub>H<sub>0.28</sub>, J. Phys. Condens, Matter 21 (2009) 175410.
- [32] I.E. Pavlov, S.I. Alyamovsky, Yu.G. Zainulin, G.P. Shveikin, Hydrogen solubility in monoxide phase of titanium, Poroshk. Metall. 10 (1975) 34–37 (in Russian).

- [33] A.A. Valeeva, A.A. Rempel, A. Pfitzner, Elimination of vacancies in titanium monoxide under high pressure in combination with high temperature, Monatsh. Chem. 146 (2015) 1205–1209.
- [34] A.A. Valeeva, A.I. Gusev, Twinning and short-range order in ordered titanium monoxide, Phys. Solid State 48 (2006) 1689–1697.
- [35] The Mention of all Commercial Suppliers in this Paper is for Clarity and Does not Imply the Recommendation or Endorsement of these Suppliers by NIST.
- [36] X'Pert Plus Version 1.0, Program for Crystallography and Rietveld Analysis, Philips Analytical B.V. © Koninklijke Philips Electronics N.V.
- [37] J.K. Stalick, E. Prince, A. Santoro, I.G. Schroder, J.J. Rush, Materials science applications of the new National Institute of Standards and Technology powder diffractometer, in: D.A. Neumann, T.P. Russel, B.J. Wuensch (Eds.), Neutron Scattering in Materials Science II, Pittsburgh, Materials Research Society, Pittsburgh, PA, 1995, pp. 101–106.
- [38] A.C. Larson, R.B. Von Dreele, General Structure Analysis System (GSAS), Los Alamos National Laboratory Report LAUR 86-748, 2000, 1–179.
- [39] B.H. Toby, EXPGUI, a graphical user interface for GSAS, J. Appl. Crystallogr. 34 (2001) 210–213.
- [40] T.J. Udovic, C.M. Brown, J. Leão, P.C. Brand, R.D. Jiggetts, R. Zeitoun, T.A. Pierce, I. Peral, J.R.D. Copley, Q. Huang, D.A. Neumann, R.J. Fields, The design of a bismuth-based auxiliary filter for the removal of spurious background scattering associated with filter-analyzer neutron spectrometers, Nucl. Instrum. Methods A 588 (2008) 406–413.
- [41] V.F. Sears, Neutron scattering lengths and cross sections, Neutron News 3 (1992) 26–37.
- [42] A.A. Rempel, W. van Renterghem, A.A. Valeeva, M. Verwerft, S. Van den Berghe, In situ disordering of monoclinic titanium monoxide Ti<sub>5</sub>O<sub>5</sub> studied by transmission electron microscope TEM, Sci. Rep. 7 (2017) 10769.
- [43] B.O. Marinder, Ordered, defective structures of titanium monoxide, the antianatase structure and related structures described through an open packing on cube units (die packing), Chem. Scr. 18 (1981) 169–175.
- [44] D. Watanabe, J.R. Castles, A. Jostsons, A.S. Malin, The ordered structure of TiO, Acta Crystallogr 23 (1967) 307–313.
- [45] A.A. Valeeva, S.Z. Nazarova, A.A. Rempel, In situ study of atomic-vacancy ordering in stoichiometric titanium monoxide by the magnetic susceptibility, JETP Lett. 101 (2015) 258–263.
- [46] D. Richter, R. Hempelmann, R.C. Bowman, Dynamics of hydrogen in intermetallic hydrides, in: L. Schlapbach (Ed.), Hydrogen in Intermetallic Compounds II, Springer, Berlin, 1992, pp. 97–163.
- [47] D.K. Ross, Neutron scattering studies of metal hydrogen systems, in: H. Wipf (Ed.), Hydrogen in Metals III, Springer, Berlin, 1997, pp. 153–214.
- [48] R.G. Barnes, Nuclear magnetic resonance in metal hydrogen systems, in: H. Wipf (Ed.), Hydrogen in Metals III, Springer, Berlin, 1997, pp. 93–151.
- [49] R. Göring, R. Lukas, K. Bohmhammel, Multipulse NMR investigation of band structure in titanium hydride: proton Knight shift and spin-lattice relaxation, J. Phys. C Solid State Phys. 14 (1981) 5675–5687.