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Placement of H atoms in the crystal lattice of cubic titanium oxyhydride: simulation and diffraction experiment

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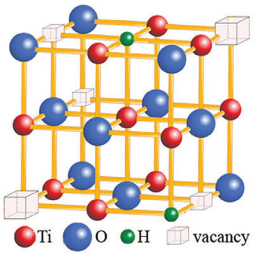
Possible models for the arrangement of hydrogen atoms in the sites of the cubic lattice of titanium oxyhydride TiO_yH_p with vacancies in the metallic and nonmetallic sublattices are considered for the first time. It has been established that interstitial H atoms in oxyhydrides occupy vacant octahedral sites 4(*b*) of the oxygen sublattice. No displacement of H atoms in tetrahedral sites 8(*c*) is observed.



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Nonstoichiometric compounds MX_y (M = Ti, Zr and Nb; X = C, N and O) with a *B*1-type structure can absorb hydrogen from the gas phase, forming ternary compounds MX_yH_x. As a rule, hydrogen atoms occupy vacant octahedral sites 4(*b*) of the nonmetallic sublattice.[1–3]

Due to their small size, H atoms can occupy, along with vacant octahedral sites of the nonmetallic sublattice, also tetrahedral interstices. The possible placement of hydrogen atoms in tetrahedral interstices follows from the fact that the relative content *p* of hydrogen can exceed the concentration $(1 - y)$ of structural vacancies in the carbon sublattice of some cubic carbide hydrides MC_yH_p ($TiC_{0.64}H_{0.38}$ and $NbC_{0.77}H_{0.32}$–$NbC_{1.00}H_{0.25}$).[4]

To date, there are no published data on the position of H atoms in cubic titanium oxyhydrides TiO_yH_p. Meanwhile, cubic titanium monoxides with double defectiveness and a wide homogeneity range from $TiO_{0.80}$ to $TiO_{1.25}$ and their oxyhydrides are promising materials (especially in the nanocrystalline state) for hydrogen technology, photocatalysis and water purification.[5]

Figure 1 shows the position of sites 4(*a*), 4(*b*) and 8(*c*) in the model structure of titanium oxyhydride TiO_yH_p ($Ti_xO_zH_{px}$), which crystallizes in a cubic system with space group $Fm\bar{3}m$. Two variants of the simulated placement of H atoms for the cubic Ti_xO_z monoxide can be proposed, allowing the possible introduction of hydrogen into the octahedral and tetrahedral interstices of the cubic lattice. In the first model, corresponding to the *B*1-type cubic structure, hydrogen can occupy only vacant sites 4(*b*) of the oxygen sublattice. In the second model, a part of hydrogen atoms can occupy vacant sites 4(*b*) of the oxygen sublattice, and the remaining H atoms statistically fill the tetrahedral interstices, *i.e.*, sites 8(*c*). This model corresponds to a cubic structure (space group $Fm\bar{3}m$) of type *D*0_3.

Let us consider what crystallographic sites hydrogen can occupy in titanium oxyhydrides and what changes can be observed in X-ray diffraction patterns (XRD) and neutron diffraction patterns of titanium oxyhydrides when H atoms are located only in sites 4(*b*) or in sites 4(*b*) and 8(*c*) simultaneously. For this, we find the structure factors F^2 for titanium monoxide $Ti_xO_z \equiv TiO_y$ ($y = z/x$) with the *B*1 structure, titanium oxyhydride $Ti_xO_zH_{px} \equiv TiO_yH_p$ with the *B*1 structure and for oxyhydride $Ti_xO_zH_{px} \equiv Ti_xO_zH^{4(b)}_{(p-q)x}H^{8(c)}_{qx}$ with the *D*0_3 structure.

The structure factor F^2 for titanium monoxide Ti_xO_z with structure *B*1 has the form:

$$F^2_{B1}(hkl) = \left\{xf_{Ti}\left[1+\cos\pi(h+k)+\cos\pi(h+l)+\cos\pi(k+l)\right]+ \right.$$
$$\left. + zf_O\left[\cos\pi(h+k+l)+\cos\pi h+\cos\pi k+\cos\pi l\right]\right\}^2. \qquad (1)$$

In titanium oxyhydride $Ti_xO_zH_{px}$ with the *B*1 structure, sites 4(*a*) are occupied by Ti atoms with probability *x*, and sites 4(*b*) are occupied by O and H atoms with probabilities *z*

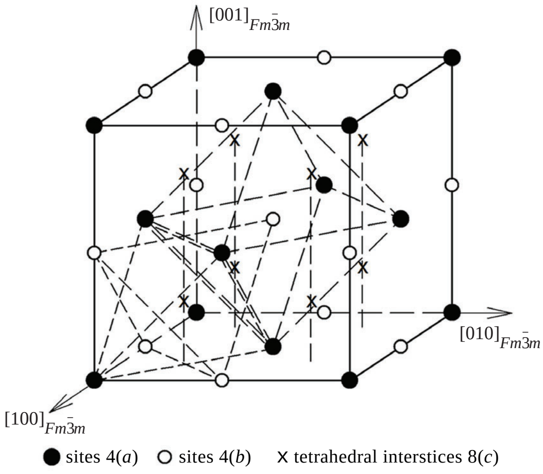

Figure 1 Model structure of non-stoichiometric cubic (space group $Fm\bar{3}m$) titanium oxyhydride TiO_yH_p ($Ti_xO_zH_{px}$), demonstrating sites 4(*a*) randomly occupied by Ti atoms, sites 4(*b*) randomly occupied by O atoms and sites 8(*c*), which are centers of tetrahedral interstices in the Ti or O sublattices.

and *px*, respectively. Allowing this, the structure factor F^2 for oxyhydride $Ti_xO_zH_{px}$ is

$$F^2_{B1}(hkl) = \{xf_{Ti}[1 + \cos\pi(h+k) + \cos\pi(h+l) + \cos\pi(k+l)] + \\ + (zf_O + pxf_H)[\cos\pi(h+k+l) + \cos\pi h + \cos\pi k + \cos\pi l]\}^2. \quad (2)$$

In equations (1) and (2), f_{Ti}, f_O and f_H are the radiation scattering factors for Ti, O and H atoms, respectively.

If hydrogens in oxyhydride $Ti_xO_zH_{px}$ can occupy vacant sites of the oxygen sublattice [sites 4(*b*)] and tetrahedral interstices [sites 8(*c*)], then sites 4(*a*) are statistically occupied by Ti atoms with probability *x*, sites 4(*b*) are statistically occupied by O and H atoms with probabilities *z* and $(p - q)x$, respectively, and sites 8(*c*) are statistically occupied by H atoms with probability $qx/2$. With allowance for the coordinates of sites 4(*a*), 4(*b*) and both 8(*c*) with the probabilities of their occupation by Ti, O and H atoms, the structure factor F^2 of a disordered cubic oxyhydride with the $D0_3$ structure is

$$F^2_{D0_3}(hkl) = x^2\Big\{f_{Ti}[1 + \cos\pi(h+k) + \cos\pi(h+l) + \cos\pi(k+l)] + \\ + [yf_O + (p-q)f_H][\cos\pi(h+k+l) + \cos\pi h + \cos\pi k + \cos\pi l] + \\ + \frac{q}{2}f_H\Big[\cos\frac{\pi}{2}(h+k+l) + \cos\frac{\pi}{2}(3h+3k+l) + \cos\frac{\pi}{2}(3h+k+3l) + \\ + \cos\frac{\pi}{2}(h+3k+3l) + \cos\frac{\pi}{2}(3h+3k+3l) + \cos\frac{\pi}{2}(h+k+3l) + \\ + \cos\frac{\pi}{2}(h+3k+l) + \cos\frac{\pi}{2}(3h+k+l)\Big]\Big\}^2 + \\ + x^2\Big\{\frac{q}{2}f_H\Big[\sin\frac{\pi}{2}(h+k+l) + \sin\frac{\pi}{2}(3h+3k+l) + \sin\frac{\pi}{2}(3h+k+3l) + \\ + \sin\frac{\pi}{2}(h+3k+3l) + \sin\frac{\pi}{2}(3h+3k+3l) + \sin\frac{\pi}{2}(h+k+3l) + \\ + \sin\frac{\pi}{2}(h+3k+3l) + \sin\frac{\pi}{2}(3h+k+l)\Big]\Big\}^2. \quad (3)$$

It can be seen from equations (2) and (3) that filling sites 8(*c*) with H atoms does not lead to the appearance of new diffraction reflections but only slightly changes the values of the structure factors. Therefore, disordered cubic oxyhydrides $Ti_xO_zH_{px}$ of structures *B*1 and $D0_3$ have the same set of diffraction reflections. The X-ray scattering factor of H atoms is very small compared to those of Ti and O atoms; therefore, the introduction of hydrogen has little effect on the intensity of X-ray reflections.

The situation is quite different in the case of neutron diffraction measurements. The coherent neutron scattering lengths for Ti, O and H nuclei are -3.348×10^{-15}, 5.803×10^{-15} and -3.742×10^{-15} m, respectively.[6] The neutron scattering lengths f_{Ti} and f_O are opposite in sign; therefore, the structure factors for even reflections are very small compared to the structure factors for odd reflections. Due to the negative scattering length of neutrons for ^{1}H nuclei, the incorporation of hydrogen into titanium monoxide leads to an additional relative decrease in the structure factors F^2 for even reflections (200), (220), (222), (400), (420) and (422) compared to factors F^2 for odd reflections (111), (311), (331) and (511). When hydrogen is introduced only into vacant sites 4(*b*), the structure factors F^2 for all even reflections are $16x^2(f_{Ti} + yf_O + pf_H)^2$. If hydrogen atoms also occupies sites 8(*c*), and the $Ti_xO_zH^{4(b)}_{(p-q)x}H^{8(c)}_{qx}$ oxyhydride has the structure $D0_3$, then the structure factors $F^2 = 16x^2(f_{Ti} + yf_O + pf_H)^2$ for even reflections (*hkl*) with $(h + k + l) = 4n$ (where *n* is an integer) become less than the structure factors $F^2 = 16x^2[f_{Ti} + yf_O + (p - 2q)f_H]^2$ for other even reflections. Therefore, refinement of the structure by analyzing the intensity ratio of neutron diffraction reflections makes it possible to determine what sites hydrogen occupies in titanium oxyhydride.

To determine the crystal lattice sites occupied by hydrogen atoms in titanium oxyhydrides, quenched disordered monoxide $TiO_{0.72}$ ($Ti_{0.95}■_{0.05}O_{0.69}□_{0.31}$) with structural vacancies ■ and □ in the titanium and oxygen sublattices, respectively, was synthesized. Detailed conditions for the synthesis of titanium monoxide in the disordered and ordered states were described earlier.[7] The quenched sample contained only the disordered cubic TiO_y phase with the *B*1-type structure and a lattice parameter of 0.41934 nm. The hydrogenation of quenched disordered cubic titanium monoxide TiO_y was carried out in a Sieverts-type vacuum system in hydrogen at atmospheric pressure and a temperature of 973 K. The crystal structure of titanium monoxide Ti_xO_z and hydrogenated samples $TiO_yH_p \equiv Ti_xO_zH_{px}$ was determined by X-ray and neutron diffraction.[†]

The crystal structure, vibrational spectra and mobility of H atoms in hydrogenated titanium monoxides TiO_yH_p with vacancies in the metallic and nonmetallic sublattices were investigated in our previous work.[9] In this work, possible models for the placement of H atoms in the sites of the cubic lattice of titanium oxyhydride are theoretically considered, taking into account the previously obtained experimental results.[9]

Cubic (space group $Fm\bar{3}m$) oxyhydride $TiO_{0.72}H_{0.30}$ with a lattice parameter of 0.42076 nm was formed as a result of the hydrogenation of disordered titanium monoxide $TiO_{0.72}$ (Figure 2).[9] The increase in the lattice parameter from 0.41934 to

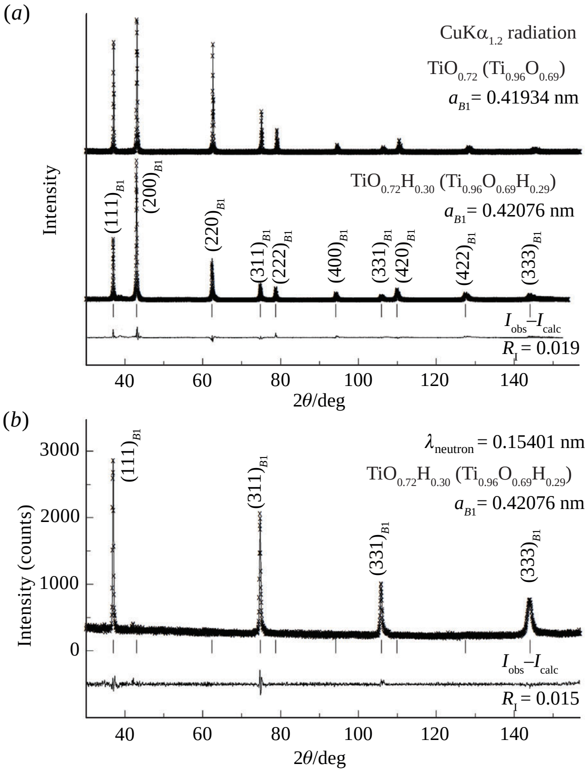

Figure 2 (*a*) XRD patterns of initial disordered cubic (space group $Fm\bar{3}m$) titanium monoxide $TiO_{0.72}$ ($Ti_{0.96}O_{0.69}$) and titanium oxyhydride $TiO_{0.72}H_{0.30}$ ($Ti_{0.96}O_{0.69}H_{0.29}$). (*b*) Neutron diffraction pattern of titanium oxyhydride $TiO_{0.72}H_{0.30}$ ($Ti_{0.96}O_{0.69}H_{0.29}$).[9] Designations: × – experimental data, solid line – calculated data, vertical dashes – diffraction reflections of disordered cubic titanium oxyhydride $TiO_{0.72}H_{0.30}$ with *B*1-type structure. The lower curves in (*a*) and (*b*) show the differences ($I_{obs} - I_{calc}$) between the observed and calculated diffraction patterns of titanium oxyhydride $TiO_{0.72}H_{0.30}$.

[†] The structures of Ti_xO_z and TiO_yH_p were determined by the Bragg–Brentano method on a Shimadzu XRD-7000 diffractometer using $CuK\alpha_{1,2}$ radiation, and the distribution of H atoms in TiO_yH_p was established by neutron diffraction on a BT18 high-resolution powder diffractometer[8] at the NIST Center for Neutron Research (Gaithersburg, MD, USA) with neutron wavelength $\lambda = 0.15402$ nm.

0.42076 nm is a consequence of the introduction of H atoms into the crystal lattice of the TiO_y monoxide.

Refinement of the structure of the single-phase $TiO_{0.72}H_{0.30}$ oxyhydride using the X'Pert Plus software[10] and the F^2 structure factors gave the following results. The refinement of the neutron diffraction pattern [Figure 2(*b*)] in the model with the *B*1 structure resulted in the following Rietveld agreement factors: $R_{\rm exp} = 0.067$, $R_{\rm p} = 0.055$, $R_{\rm wp} = 0.072$ and $R_{\rm I}$ ($R_{\rm Bragg}$) = 0.015. The use of the $D0_3$-type structure model with a quarter of all H atoms located in tetrahedral interstices led to degradation of convergence: $R_{\rm exp} = 0.069$, $R_{\rm p} = 0.056$, $R_{\rm wp} = 0.073$ and $R_{\rm I} = 0.018$. The placement of all hydrogen atoms in tetrahedral sites 8(*c*) worsened the convergence of the experimental and theoretical neutron diffraction patterns even more. Thus, the refinement of the structure of the $TiO_{0.72}H_{0.30}$ oxyhydride according to X-ray diffraction and neutron diffraction data showed that this oxyhydride has the cubic (space group $Fm\bar{3}m$) structure of the *B*1 type, in which all hydrogen atoms are in sites 4(*b*).

The determination of the structure of titanium oxyhydrides TiO_yH_p showed that the oxyhydrides retain the B1-type crystal lattice of the initial cubic monoxides. Interstitial hydrogen atoms occupy vacant octahedral sites 4(*b*) of the oxygen sublattice of cubic titanium oxyhydrides, while hydrogen atoms are not located in tetrahedral sites 8(*c*).

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