**In situ Neutron Diffraction on D$_x$Nb$_2$O$_5$**

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D$_x$Nb$_2$O$_5$ is thermodynamically unstable. Therefore, neutron diffraction measurements were performed in the electrochemical cell used for the intercalation of deuterium into sintered Nb$_2$O$_5$ powder samples. Diffraction patterns were recorded at equilibrium potentials of −443, −428, −332 and −197 mV vs. NHE (corresponding to $x = 0.232$, $x = 0.23$, $x = 0.21$ and $x = 0.06$). The structural changes in Nb$_2$O$_5$ caused by the deuterium insertion are small but could be determined reproducibly. The lattice parameters of the host lattice exhibit a characteristic dependence on the deuterium content of the bronze. A model has been developed for the partially inhomogeneous distribution of the deuterium in the Nb$_2$O$_5$ unit cell, which explains the changes of the peak intensities observed in the low angle region ($6^\circ < 2\theta < 18^\circ$).

**Introduction**

The formation of the niobium hydrogen bronze H$_x$Nb$_2$O$_5$ ($0 < x < 0.25$) during electrochemical reduction of Nb$_2$O$_5$ is indicated by a color change from white to deep blue. Thin film electrodes [1-5] and pressed powder samples [6] of this material have been investigated, because of the possible use of Nb$_2$O$_5$ in electrochromic devices. It has been shown that the insertion is not a surface but a bulk effect [7]:

$$x \text{H}^+ + x \text{e}^- + \text{Nb}_2\text{O}_5 \rightarrow \text{H}_x\text{Nb}_2\text{O}_5.$$  

The insertion of hydrogen does not change the structure of Nb$_2$O$_5$ significantly, as has been demonstrated by in situ X-ray diffraction [8]. The problem of the crystallographic structure description of the bronze can thus be reduced to a determination of the location of the hydrogen in the unit cell of the host oxide. Neutron diffraction is the most suitable method for this purpose, but it requires the replacement of hydrogen (a strong incoherent scatterer) by deuterium.

The measurements were performed with the high-resolution two-axis neutron diffractometer D1A at the ILL in Grenoble, France, using a neutron wavelength $\lambda = 1.911$ Å.

**Experimental**

The electrode potential of H$_x$Nb$_2$O$_5$ is less than −400 mV vs. NHE [6], which means that the bronze is thermodynamically unstable with respect to decompo-

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Fig. 2. Equipment of the electrochemical cell for neutron diffraction experiments.

sition into Nb$_2$O$_5$ and gaseous hydrogen. Therefore, the neutron experiments had to be carried out in situ, i.e. in an electrochemical cell (Fig. 1) under potentiostatic control. During the experiment the electrolyte (1 N D$_2$SO$_4$ in D$_2$O; D$_2$SO$_4$, Fluka, 96-98 % in D$_2$O, > 99.5 % isotopic purity; D$_2$O, Alfa, 99.8 % isotopic purity) was pumped (pump: Minipuls 3, Gilson) through the cell, carrying away the oxygen, evolved at the counter electrode situated far away from the sample (Fig. 2). Afterwards the electrolyte flowed through 2 washing bottles in series, where the oxygen is purged with nitrogen, in order to prevent a reoxidation of the bronze on recycling.

The Nb$_2$O$_5$ sample was pressed on a Pt ring, which was insulated with silicone from the electrolyte and carefully kept out of the neutron beam. The cell was sealed by two polyethylene foils, which also served as windows for the neutron beam (Fig. 1). The circular area of the sample exposed to the neutron beam had a c.d. of 2.8 cm. The samples were prepared by pressing pure Nb$_2$O$_5$ powder (Alfa, 99.9 %) to tablets (2 GPa, c. d. 42 mm, thickness 5 mm, weight 18 g), which were then heated in air to 1250 °C for 3 d in order to obtain pure H-Nb$_2$O$_5$ [9]. The density of the samples was $\rho_{\text{d,h}} = (2.6 \pm 0.1)$ g/cm$^3$, which is about 57 % of the density of pure H-Nb$_2$O$_5$. It was demonstrated gravimetrically that the pores in the sample could be completely filled up with electrolyte (accuracy of the method $\pm 1 \%$).

The pure Nb$_2$O$_5$ sample was loaded with hydrogen galvanostatically in the closed apparatus. When the potential reached $E \approx -400$ mV vs. NHE, it was stabilized by potentiostatic control. After 20 h the current became constant indicating stationary equilibrium. In subsequent experiments different potentials, corresponding to other H contents, were adjusted in the same manner. Two sets of equivalent apparatus were used alternately for an efficient utilisation of the allocated beam time.

We recorded 4 diffraction patterns of the samples at equilibrium potentials of $(-443 \pm 5)$, $(-428 \pm 5)$, $(-332 \pm 6)$ and $(-197 \pm 1)$ mV vs. NHE together with one of pure Nb$_2$O$_5$ and one of the cell without a sample (blank measurement) in order to obtain information about the background. The diffraction patterns were recorded at room temperature over the range $6^\circ \leq 2\theta \leq 90^\circ$.

The refinements and simulations of the neutron diffraction patterns were performed using the Rietveld refinement program DBWS from R. A. Young [10].

**Results and Discussion**

The large background in the diffraction patterns was mainly produced by the electrolyte within the porous sample, as confirmed by the blank measurement. As in this measurement the background was increased because the volume of the absent Nb$_2$O$_5$ sample was replaced by additional electrolyte, the data for the blank measurement were multiplied by an appropriate factor, for all measurements, very close to the expected value of 0.57, and then subtracted from the sample data. For large angles, however, the observed background of all samples exceeded that of the corrected blank measurement (Fig. 3). This was caused by the double scattering in the blank measurement, with increasing angle. Therefore, in the refinement this part of the sample background was fitted using a 3rd order polynomial. Both corrections are indicated in Fig. 3.

![Fig. 3. Neutron diffractogram of D$_2$Nb$_2$O$_5$ ($E = -443$ mV vs. NHE) (+) with corrected background of the blank measurement (dots) and background caused by double scattering (dashed line).](image-url)
The crystal structure of H–Nb$_2$O$_5$ has been determined by Gatehouse and Wadsley [11]. The monoclinic unit cell (space group P2) consists of 14 formula equivalents. The structure is built up of two different ReO$_3$–like blocks of corner shared NbO$_6$ octahedra having infinite expansion in crystallographic $a$ direction and consisting of $3 \times 5$ and $3 \times 4$ octahedra in the $a$–$c$ plane, respectively. The blocks are linked together by edge sharing of the octahedra. In this way, two tetrahedral sites for niobium are produced in the unit cell, only one of which is occupied for stoichiometric reasons. Neither X–ray nor neutron diffraction yielded any evidence that this structure changes during the intercalation of H or D [8].

The differences between the neutron diffraction patterns of H–Nb$_2$O$_5$ and D$_x$Nb$_2$O$_5$ are small, but they are reproducible and appear on reducing the sample and disappear when it is re–oxidized. A change of the lattice constants was observed as a function of the D content and will be discussed below. In contrast to the equivalent X–ray diffraction patterns, the intensities of some peaks changed significantly at low diffraction angles (Fig. 4). Evidently, the observed changes in the neutron diffraction patterns are caused by the scattering of intercalated deuterium. In order to obtain information concerning the location of the intercalated deuterium (or hydrogen), the neutron diffraction patterns for different D distributions were calculated and compared with the experimental diffraction patterns. As is known for other bronzes [12], D sites in the oxide were assumed to be on the connection line between two oxygen atoms, but with the simplification that the D positions lie in the middle between them. The occupation numbers were calculated from the electrode potentials $E$ using the $E = f(x)$ dependence obtained for H$_x$Nb$_2$O$_5$ [7]. Homogeneous D distributions, where the D atoms are placed e. g. between all oxygen atoms with O–O distances $d_{O-O} \leq 3.2$ Å (Fig. 4c, 295 D positions per unit cell) lead to diffraction patterns very similar to that of pure Nb$_2$O$_5$. Therefore, it has to be concluded, that the intercalated deuterium is inhomogeneously distributed. The D positions between two oxygens with distances 2.4 Å $< d_{O-O} < 2.6$ Å could be favoured, because hydrogen bonds in such OD–O–groups are particularly strong. However, the calculated diffraction patterns for this structure do not match the experimental patterns (cf. Fig. 4c, “weight type 1”). Other D positions in the host lattice can explain the diffraction patterns better, when these are calculated for the case that either the D(1) positions indicated in Fig. 5 are occupied by one D atom each (displayed in Fig. 4c, “weight type 2”) or the D(2) positions are occupied half by the D atoms (labeled “weight type 3” in Fig. 4c), respectively. In both cases, these occupations of the D(1) and D(2) positions correspond to a D content $x'$ of the bronze D$_x$Nb$_2$O$_5$ of $x' = 0.143$. The D content corresponding to the difference between this value $x'$ and the actual value of $x \approx 0.23$ was treated as distributed homogeneously over all other sites with $d_{O-O} \leq 3.2$ Å. As it can be seen in Fig. 4c, the calculated patterns match rather well the measured data of the D$_{0.23}$Nb$_2$O$_5$ sample (see Fig. 4b) and reproduce the observed increase in scattered intensity at 6.45°, 10.32° and 12.97°, as well as the decrease...
at $2\theta = 11.9^\circ$ by both weight types. The fit quality, therefore, does not allow any preference between either. However, it is possible to say that configurations with deuterium mainly surrounding the unique Nb–free tetrahedral site of the Nb$_2$O$_5$ unit cell (see Fig. 5) are more probable than configurations where the deuterium is mainly located near an octahedral Nb–site. The peak at 9.2° (see Fig. 4b), which could be observed in all diffraction patterns with similar intensities, can neither be assigned to Nb$_2$O$_5$ nor to D$_x$Nb$_2$O$_5$, and it does not occur in the X–ray diffraction patterns. It is obviously an artefact caused by the beam stop which starts to cast a shadow on the detectors. This can be seen in Fig. 3 when looking at the sharp decrease of the scattered intensity for angles lower than 9.2°.

The lattice constants of D$_x$Nb$_2$O$_5$, which were obtained by refining the structure of pure Nb$_2$O$_5$ on the basis of the experimental diffraction patterns, are shown in Fig. 6 as a function of the electrode potential. With the exception of the points for $E = -443$ mV (see below), the lattice parameters $b$ and $c$ increase monotonically with decreasing potential (increasing D content) whereas $a$ and $\beta$ pass a minimum near $E = -200$ mV. In this potential region the shape of the $E$ vs. $t$ curves changes when measured during the decomposition of H$_x$Nb$_2$O$_5$ [7]. This correlation between the electrode potential and the structure can be interpreted by a statistical thermodynamic approach [8], which makes use of the above D distribution model.

The sample with $E = -443$ mV was under potentiostatic control for 54 h before the measurement was started whereas all other samples were equilibrated for only 12 h. As can be seen in Fig. 6, the lattice constant $b$ of the better equilibrated sample is enlarged, whereas $a$ and $c$ are diminished compared with the lattice constants of the sample at the potential $E = -428$ mV. This apparent discrepancy is due to a structural relaxation effect which has also been observed in time resolved in situ X–ray diffraction and in the electrode potential of the bronze [7].
This relaxation effect can also be interpreted by the above mentioned statistical model [8].

**Summary**

During the intercalation of deuterium structural changes of Nb$_2$O$_5$ can be reproducibly observed by neutron diffraction. The variations of the lattice constants with the D content are correlated to the electrode potential of the bronze. The deuterium distribution in the niobium hydrogen bronze D$_x$Nb$_2$O$_5$ is inhomogeneous. Simulations of the *in situ* neutron diffraction experiments gave strong indications that the deuterium atoms are mainly located near the unique Nb free tetrahedral site in the unit cell of the host lattice.