

Influence of hydrogen intercalation on the local structure around Re ions in perovskite-type ReO_3

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In-situ X-ray absorption spectroscopy at the Re L_1 and L_3 edges was used to study a modification of the local atomic and electronic structure around rhenium in perovskite-type ReO_3 upon hydrogen intercalation. The analysis of both EXAFS and XANES parts of the X-ray absorption spectra shows an evidence of the charge disproportionation phenomenon in hydrogenated rhenium trioxide.

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Rhenium trioxide ReO_3 has a cubic perovskite-type (ABO_3) structure composed of regular ReO_6 octahedra joined by vertices with the vacant perovskite A sites [1]. The $5d^1$ electronic configuration of Re^{6+} ions results in the partially filled conduction band, formed by the covalently mixed Re $5d$ and O $2p$ states [2] and explaining the metallic conductivity of ReO_3 . These conduction electrons play also the main role in the stabilization of the cubic structure of ReO_3 [3]. While many perovskites, as for example SrTiO_3 , BaTiO_3 and KNbO_3 , show upon temperature change a series of phase transitions, caused by condensation of one or more optical modes [4] and accompanied by the electronic and atomic structure changes, the structure of ReO_3 remains non-distorted at atmospheric pressure down to liquid-helium temperature [3]. However, a number of phase transitions can be induced in ReO_3 by applying external pressure [1, 5, 6] or by hydrogen insertion, that results in the formation of hydrogen rhenium bronzes H_xReO_3 [7–9].

X-ray and neutron diffraction [1,5,6] and X-ray absorption spectroscopy (XAS) [10] studies has revealed that pressure effect results in a rotation (the Re-O-Re angle changes from 180° to 160°) of ReO_6 octahedra, but the octahedra remain regular with the Re-O bond length about 1.88 ± 0.01 Å. Neutron diffraction study [9] of the hydrogen rhenium bronze $\text{D}_{1.36}\text{ReO}_3$ showed that the hydrogen insertion produces similar effect on the ReO_3 structure. In particular, for $x=1.36$ the bronze structure is composed of tilted regular ReO_6 octahedra with the Re-O-Re angle equal to 169° and the Re-O distance of about 1.90 Å [9]. More accurate information on the local atomic and electronic structure of the bronzes can be obtained using XAS, which is a structural method complimentary to diffraction. To our knowledge, no such works have been performed until now.

In this work, we present the first results of the in-situ XAS study of hydrogen intercalation into ReO_3 . The analysis of both extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) allowed us to reconstruct changes of the local environment around rhenium ions occurring upon hydrogen intercalation and provides an evidence of charge ordering at rhenium sites.

X-ray absorption spectra were recorded at the Re L_1 and L_3 -edges in transmission mode at the LURE DCI storage ring on the EXAFS-3 beam line, located at the bending magnet. The storage ring DCI oper-

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ated at the energy 1.85 GeV and the maximum stored current 316 mA. A standard transmission scheme with a Si(311) double-crystal monochromator and two ion chambers containing argon gas was used. The data were recorded during a single injection of the storage ring with an energy spacing of 2 eV and the energy resolution about 3 eV. All experiments were done at room temperature.

The sample for X-ray absorption measurements was prepared from commercial polycrystalline ReO_3 (99.9%, Prodotti Gianni), which was platinized to facilitate hydrogen intercalation. ReO_3 was mixed with boron nitride powder, and the mixture was placed in a closed boron nitride cell mounted in a chamber.

The experiments were performed in three steps. First, a helium flow was allowed to pass through the sample for 1 hour to remove air atmosphere. Next, the hydrogen was intercalated in-situ by allowing a hydrogen flow to pass through the sample for 2.5 hours. No change in the extended X-ray absorption fine structure (EXAFS) signal was observed after this time. Finally, the air flow was passed through the sample for 2 hours to oxidize it and to check for reversibility of the process. The X-ray absorption spectra were continuously measured during all the time

Thus obtained X-ray absorption spectra were treated using the EDA software package [11]. The X-ray absorption near edge structure (XANES) and EXAFS signals were extracted using conventional procedure [12]. The analysis of the EXAFS signals from the first coordination shell was performed using two sets of backscattering amplitude and phase shift functions for the Re-O atom pair: (i) the theoretical set was calculated by the ab initio FEFF8 code [13] for the ReO_3 crystal and (ii) the experimental set was extracted from the Re L_3 -edge EXAFS signal of pure ReO_3 using the Fourier filtering procedure [12, 14] and a known set of structural parameters [1, 15]: the coordination number $N=6$, the interatomic distance $R(\text{Re-O})=1.875 \text{ \AA}$ and the Debye-Waller (DW) factor $\sigma^2=0.0025 \text{ \AA}^2$. Our analysis indicated that while both sets provide with qualitatively similar results, the use of experimental backscattering amplitude and phase shift functions leads to better fitting of the experimental EXAFS signals. Therefore, only results obtained with the second set of backscattering functions will be discussed further.

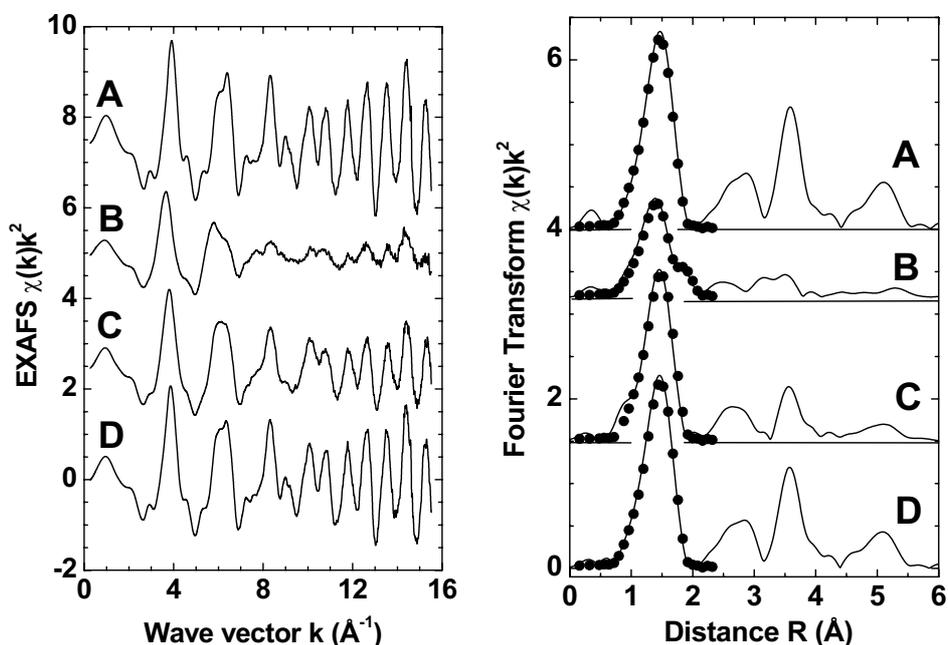


Fig. 1 Experimental Re L_3 -edge EXAFS signals $\chi(k)k^2$ (left panel) and their Fourier transforms (FTs) (right panel). The curves corresponds to (a) pure ReO_3 ; (b) H_xReO_3 after 2.5 hours of intercalation; (c) and (d) to ReO_3 during deintercalation process. The solid circles in the right panel correspond to FTs of the best-fitted theoretical EXAFS signal.

The experimental Re L_3 -edge EXAFS signals and their Fourier transforms (FTs) are shown in Fig. 1. Four main peaks, located at 0.6–2.2 Å, 2.2–3.1 Å, 3.3–4.1 Å and 4.4–5.5 Å, are present in the FTs of experimental EXAFS spectra of ReO_3 . Their origin was described in details previously [14–16]. Here we will concentrate on the first peak, corresponding to the group of 6 oxygen atoms, located in the first shell of rhenium at 1.875 Å. Note that the positions of peaks in FT differ from the true crystallographic values due to the presence of the backscattering phase shifts [12]. The shape of the first peak changes gradually upon hydrogen intercalation and it takes a double-peak shape after 2.5 hours. Besides, the remaining peaks at longer distances, corresponding mainly to the outer shells composed of rhenium atoms, also decrease significantly their amplitudes. This means that hydrogen intercalation produces strong effect on the local structure around rhenium at least up to 6 Å. The most important effect is a strong decrease of the amplitude for the peak at 3.5 Å, which corresponds to the second coordination shell of rhenium, composed of six rhenium atoms. The origin of the peak is due to several multiple-scattering contributions within Re-O-Re atomic chains [10, 16], that makes its intensity strongly angular dependent. Therefore, the observed variation of the peak amplitude is related to the change of the Re-O-Re angle between two adjacent ReO_6 octahedra [10, 16], that suggests their tilting upon hydrogen intercalation.

The EXAFS signals from the first peak were best fitted using the one-shell and two-shells Gaussian models [12]. The fitting parameters were coordination numbers (N), interatomic distances (R) and the DW factors (σ^2). Several intervals in k -space (Fig. 1) were used to estimate the errors of the structural parameters. Thus obtained theoretical EXAFS signals show very good agreement with the experimental data, and their FTs are compared in Fig. 2. The set of parameters describing the local structure around rhenium in ReO_3 before hydrogen intercalation, is $N=6.0\pm 0.4$, $R=1.871\pm 0.003$ Å, $\sigma^2=0.0022\pm 0.0007$ Å². After 2.5 hours of hydrogen intercalation, the first peak becomes a double-peak shaped and can be approximated only by the two-shells Gaussian model with parameters $N_1=3.5\pm 0.4$, $R_1=1.878\pm 0.005$ Å, $\sigma_1^2=0.003\pm 0.001$ Å² and $N_2=3.4\pm 0.5$, $R_2=2.063\pm 0.006$ Å, $\sigma_2^2=0.006\pm 0.001$ Å². Finally, after oxidation of the sample, the EXAFS signal turns back to the initial one (Fig. 1), with the close values of structural parameters indicating that intercalation and de-intercalation processes are reversible.

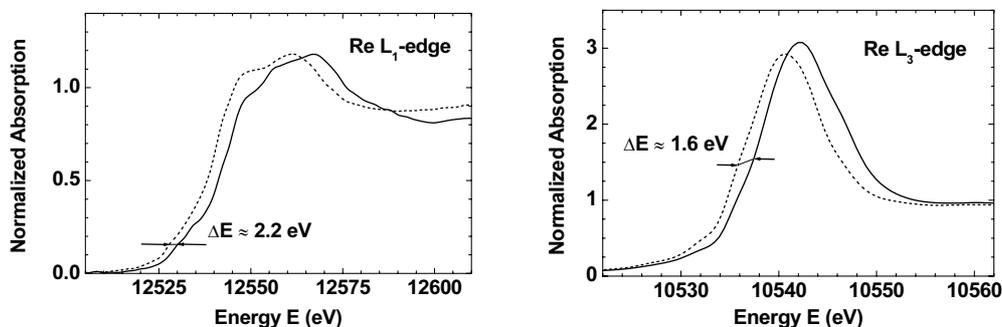


Fig. 2 Experimental Re L_1 and L_3 edges XANES signals in pure ReO_3 (solid line) and H_xReO_3 after 2.5 hours of intercalation (dashed line). The edge shift, measured at the half height of the transition to lowest empty $5d$ -states, is about -2.2 ± 0.3 eV for L_1 -edge and -1.6 ± 0.2 eV for L_3 -edge.

The presence of the two shells in hydrogen intercalated ReO_3 can be explained in two ways: either the ReO_6 octahedron becomes strongly distorted with about N_1 short bonds and N_2 long bonds or at least two different Re sites co-exist in the structure. In the latter case, the ratio between two sites is N_2/N_1 . The interesting fact is that the values of R_1 and σ_1^2 for the first shell are very close to that in Re^{6+}O_3 , whereas the second shell has the value of the Re-O distance R_2 close to that one finds in Re^{4+}O_2 , having four short bonds (1.94 Å) and two long bonds (2.11 Å) with the average value ~ 2.0 Å [17]. Note also that the DW factor σ_2^2 is larger than σ_1^2 meaning either weaker bond or the presence of the Re-O distances distribution in the second shell. If ReO_6 octahedra becomes distorted upon hydrogen intercalation then this effect should be observed at the Re L_1 -edge, which is sensitive to the coordination polyhedra symmetry [18].

The experimental XANES signals at the Re L_1 and L_3 edges are shown in Fig. 2. In both cases a shift of the absorption edge to the smaller energies is observed and is attributed to the lowering of the mean valence state of rhenium ions upon hydrogen intercalation, according to the reaction $\text{Re}^{6+}\text{O}_3 + x\text{H} \rightarrow \text{H}_x\text{Re}^{(6-x)+}\text{O}_3$. The value of the shift differs for two edges due to different interaction between the core hole and the excited electron: at the L_1 -edge the electron is transferred from $2s$ level to np -states, whereas at the L_3 -edge the transition is from $2p_{3/2}$ level to nd -states. The important feature at the L_1 -edge is the so-called pre-edge peak, located at ~ 12535 eV in ReO_3 (left panel in Fig. 2). It is due to dipole forbidden transition $2s \rightarrow 5d$, and one expects that the pre-edge peak intensity increases upon local symmetry lowering, for example, in distorted octahedral or tetrahedral environment [18]. The pre-edge peak is visible just as a shoulder in ReO_3 and becomes even weaker upon hydrogen intercalation. This strongly suggests that no octahedra distortion occurs. Thus, the analysis of XANES supports the two sites model. Finally, one can also consider a model, based on simultaneous co-existence of two crystallographic phases as ReO_3 and ReO_2 . However, it can be excluded since otherwise the amplitude of the second shell peak at 3.5 \AA in FT for H_xReO_3 (curve (b) in right panel of Fig. 1) would be at least 50% of that in ReO_3 .

To conclude, the results obtained from the analysis of the Re L_1 and L_3 edges EXAFS and XANES signals show an evidence of the charge disproportionation phenomenon [19, 20] ($2\text{Re}^{5+} \rightarrow \text{Re}^{6+} + \text{Re}^{4+}$) in hydrogenated rhenium trioxide. The two Re-O distances determined by EXAFS correspond to two different Re sites, both having nearly regular octahedral coordination and co-existing in the proportion equal to $N_1:N_2 \approx 1:1$. The first site is similar to that in pure ReO_3 with Re ions, having valence state $6+$, whereas the second site is similar to that in ReO_2 with Re ions, having valence state $4+$. The Re^{4+}O_6 octahedra are larger by $\sim 0.18 \text{ \AA}$ than the Re^{6+}O_6 octahedra, that leads to the octahedra tilting with roughly estimated Re-O-Re angle equal to about 144° (here we used $R(\text{Re-Re}) \approx 3.75 \text{ \AA}$ as in $\text{H}_{0.38}\text{ReO}_3$ [8] and $\text{D}_{1.36}\text{ReO}_3$ [9]).

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