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Nexafs study of the O_2–Yb–Si(111) nanofilm system

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The near-edge X-ray absorption fine structure of the adsorbed oxygen layer on the ytterbium nanofilm has been studied. It is shown that oxygen is chemisorbed in the form that is close to singly charged O_2^- ions. The O–O bond length in such ions is determined (1.33 Å). X-ray dichroism of chemisorbed molecules is detected. It is due to the orientation of intramolecular σ^* orbitals predominantly along the normal to the ytterbium surface.

Keywords: X-ray absorption, near-edge fine structure, nanoadsorbent, chemisorption, oxygen, ytterbium.

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The interest in nanoadsorbents has been on the rise in recent years [1–3]. They differ fundamentally from conventional massive substrates in that a significant fraction of the total number of atoms in the sample is located on its surface (up to 50 % and higher). This opens up opportunities for targeted control of the properties of a nanoadsorbent as a whole with the application of surface phenomena (in particular, chemisorption of molecules capable of forming strong bonds with the surface).

It has been demonstrated recently [4] that a number of important modifications may occur in ytterbium nanofilms with a thickness ranging from ~ 0.4 to 12 nm when certain molecules with lone-pair electrons (CO or O_2) are applied to them. Specifically, valence transition $Yb^{2+} \rightarrow Yb^{3+}$ [4], the emergence of a band gap (metal–semiconductor transition) [5], a change in the electron mean free path [6], and strengthening of interatomic bonds [5] were observed in nanoadsorbents. At the same time, the electronic properties, conformation, and orientational symmetry of molecules in such systems remain understudied, which makes it difficult to construct a generalized model of them. The indicated data are also important in the context of gaining a deeper understanding of the processes of interaction of oxygen with rare earth metals [7].

The aim of the present study is to obtain information regarding the electronic structure, adsorption geometry, and bond length of O_2 molecules on the surface of a Yb-nanoadsorbent. NEXAFS (near-edge X-ray absorption fine structure) spectroscopy was chosen as a means to reach this goal. This method is known [8–10] to be very sensitive to multiple photoelectron scattering resonances in chemisorbed molecules with low atomic numbers of elements (O_2 included). This allows one to use the near-edge fine structure (K edge) of X-ray absorption spectra to identify the electronic state and the chemical nature of adsorbed oxygen. The above intramolecular resonances arise after photoexcitation of electrons from the K shell (core $1s$ level) to unoccupied molecular orbitals and/or quasi-bound continuum states and are governed by the selection rules for dipole transitions. Therefore, the analysis of line intensities in NEXAFS spectra also allows one to determine the orientation of molecules on the surface. An O_2 molecule in the $^3\Sigma$ ground state has one unpaired electron in each of the two antibonding $1\pi_g^*$ orbitals [11]. This configuration should feature a resonance due to the $1s \rightarrow 1\pi_g^*$ transition, and its intensity should be maximized when electric field strength vector **E** of synchrotron radiation is parallel to the π^*- orbital of the molecule. Another resonance in the absorption spectra for O_2 should emerge upon excitation of a $1s$ electron to the antibonding $3\sigma_u^*$-orbital that is located slightly higher in energy than the $1\pi_g^*$ level. The amplitude of this resonance will reach its maximum when vector **E** is directed along the internuclear axis of the molecule (i.e., parallel to the σ^* orbital).

All experiments were carried out *in situ* at the „NANOFES“ station [12] of the „KISI-Kurchatov“ specialized synchrotron radiation source at the National Research Center „Kurchatov Institute“ (Moscow). A single-crystal silicon sample doped with phosphorus (n-type, 7.5 $\Omega \cdot$ cm) with a (111) surface orientation was used as a substrate for ytterbium nanofilms. To clean it, the crystal was heated to 1500–1530 K under ultra-high vacuum. Bright reflections of the superlattice (7×7) were observed in the low-energy electron diffraction pattern recorded after heating. Ytterbium atoms were deposited from a Knudsen cell made of tantalum and heated by a laser beam at a residual pressure of $< 1 \cdot 10^{-8}$ Torr in the vacuum chamber. The deposition rate was one monolayer (0.38 nm) per minute. The temperature of the Si substrate was maintained at ~ 290 K in the process of deposition, which provided an opportunity to grow ytterbium nanofilms with high thickness uniformity and a chemically sharp interface with

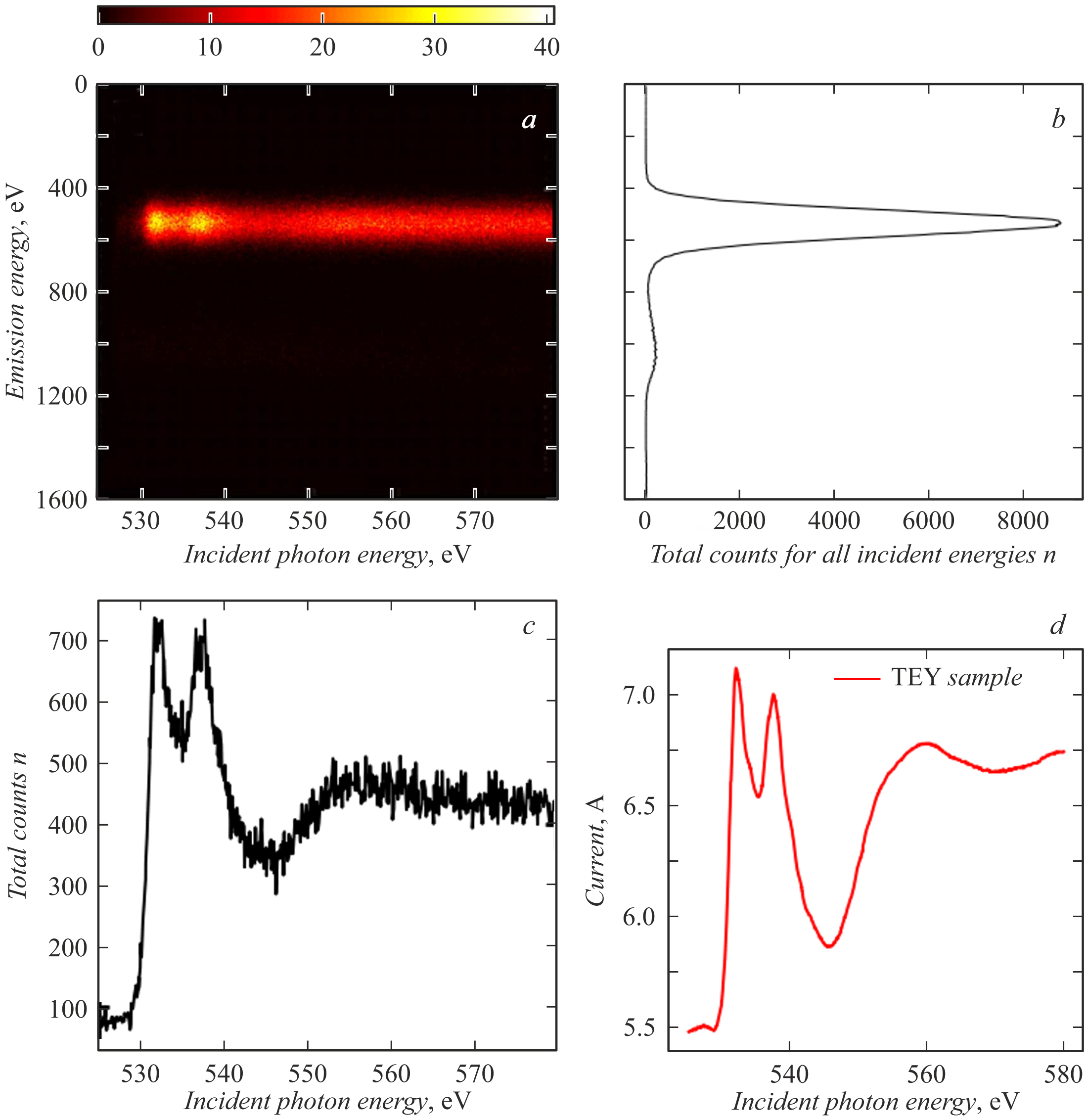

Figure 1. NEXAFS spectra for the O_2–Yb–Si(111) structure. The angle of incidence of primary photons is $\theta = 15^\circ$. The thickness of the ytterbium nanofilm is 6.1 nm. See details in the text.

silicon [13]. Oxygen adsorption was carried out at the same temperature and a partial O_2 pressure of $5 \cdot 10^{-7}$ Torr. The dose was 100 L (Langmuir), which provided saturating coverage of the adsorbed layer [14]. Valence transition $2+ \to 3+$ in the O_2–Yb–Si(111) structures was monitored by photoelectron $4f$ spectra.

Two different techniques were used to obtain absorption spectra. In the first method, the dependence of the total electron yield (TEY), which was monitored by the neutralization current in the sample circuit, on incident photon energy $h\nu$ was recorded. The other technique involved monitoring the fluorescence output in the photon counting mode with a silicon sensor located near the sample surface. These two types of measurements were carried out simultaneously. The resolution in incident photon energy near the K edge of the oxygen absorption band (~ 531 eV) was ~ 0.10–0.11 eV.

It is clear that the near-edge fine structure of NEXAFS spectra should depend on whether oxygen molecules decompose into atoms on the nanoadsorbent surface. In the case of non-dissociative adsorption, the main features of the spectral line are resonances emerging due to the $1s \to 1\pi_g^*$ and $1s \to 3\sigma_u^*$ transitions in molecules. If adsorption is dissociative, such resonances are not observed, and the shape of spectra is governed by the density of states above the Fermi level induced by the bonds of O atoms with ytterbium. Figure 1 shows the NEXAFS results for the O_2–Yb–Si(111) structure with a nanofilm thickness of 16 ML (6.1 nm). The angle of incidence (θ) of photons on the sample relative to the normal to the surface (equivalent to the angle between the surface plane and vector **E**) was 15°. The dependence of the fluorescence yield on the energy of incident (horizontal axis) and emitted (vertical axis) photons (Fig. 1, a) and the dependence of the total yield of fluorescence photons on their energy (Fig. 1, *b*) are shown in the upper panels of this figure. These dependences illustrate the main features of the absorption band for the studied structure. It can be seen that its edge (absorption threshold) is located close to $h\nu \approx 531$ eV, which corresponds to the energy of the *K*-oxygen shell. Two bright spots (maxima of fluorescent output) are discernible in the immediate vicinity of the edge of this band (Fig. 1, *a*). Their positions correspond to the energy values characteristic of scattering resonances in O_2 molecules. The maximum with an energy of 532.0 eV is induced by the $1s \rightarrow 1\pi_g^*$ transition. Another maximum at $h\nu = 537.3$ eV is associated with transition $1s \rightarrow 3\sigma_u^*$. These results suggest that oxygen on the surface is molecular and its atoms are not found within the nanofilm.

A more detailed view of the near-threshold region of the spectra is presented in the lower panels of Fig. 1, where the dependences of total fluorescence (Fig. 1, *c*) and electron (Fig. 1, *d*) yields on the energy of primary photons are shown. As can be seen, the curves have a similar shape: each features two main resonances at $h\nu = 532.0$ and 537.3 eV, a minimum near the ionization threshold of an O_2 molecule (12.07 eV), and an absorption step at higher energies, where the absorption intensity depends only weakly on the wavelength of incident radiation. Rydberg states [15] and/or scattering resonances involving nanoadsorbent atoms may contribute to the spectra near the minimum. A more detailed analysis of the spectra will be performed in future studies.

Another important conclusion from the results presented in Fig. 1 concerns the adsorption configuration and electronic state of oxygen molecules on the ytterbium surface. It was demonstrated in [16] that the energy of the σ^* resonance depends linearly on the bond length in an O_2 molecule. The O–O bond length for adsorbed oxygen was estimated in the present study based on this reasoning. The obtained estimate is 1.33 Å. This value exceeds the corresponding value for a neutral O_2 molecule (1.21 Å), is lower than the value for a doubly charged $(O_2)^{2-}$ molecular ion (1.49 Å), and is closest to the value for a singly charged O_2^- ion (1.26 Å) [17]. The obtained data imply that the formation of a monomolecular oxygen layer in the studied system is accompanied by charge transfer from the ytterbium film to chemisorbed acceptor molecules. This conclusion agrees completely with the results of measurements of the work function of $O_2-Yb-Si(111)$ structures [14]. The migration of electrons leads to an increase in charge density at the $1\pi_g^*$- orbitals of molecules and stretching of the O–O bonds in them.

A similar deformation of oxygen molecules was observed in the process of their chemisorption on Pt(111) [16] and Ni(100) [18] surfaces. In these systems, the σ^* resonance was observed at energies of 538.0 and 539.0 eV, respectively. The results obtained for the O_2/Ag(110) [16] system stand somewhat apart. Its energy of the σ^* resonance is 532.6 eV (corresponding to the O–O bond length of 1.47 Å in the molecule), and the π^* resonance is lacking completely. This is attributable to the fact that a chemisorbed molecule „lies“ on the Ag(110) surface in a horizontal position, forming π bonds with the substrate, and its $1\pi_g^*$ orbitals get filled completely (as in an H_2O_2 hydrogen peroxide molecule [19,20]). According to the Pauli principle, the $1s \rightarrow 1\pi_g^*$ transition is forbidden in such a molecule.

What is then the orientation of O_2 molecules on the surface of ytterbium nanofilms? To answer this question, NEXAFS spectra were recorded at different angles $\theta = 0$, 15, and 55°. They are shown in Fig. 2. Each curve was normalized to the amplitude of the peak at 532.0 eV (π^* resonance). It is evident that if molecules are positioned vertically on the surface, their σ^*- orbital is oriented perpendicular to the surface and the intensity of the peak at $h\nu = 537.3$ eV (σ^*- resonance) will increase with increasing θ. In the contrary case (when molecules „lie“ on the surface), an increase in angle θ should be accompanied by a reduction in amplitude of the peak corresponding to the σ^* resonance. It can be seen from Fig. 2 that NEXAFS spectra obtained at different values of θ do indeed feature an angular dependence (X-ray dichroism). The σ^*- resonance intensity increases with increasing angle. This implies that the preferred orientation of molecules on the surface is vertical. It should also be noted that the dependence of spectra on θ is rather weak. This is attributable to the fact that the ytterbium nanofilm surface in the present study has a higher roughness than pure atomically smooth single-crystal substrates. The latter implies that the angular dependences of resonances are affected not only by the orientation of molecules in the adsorbed layer, but also by the morphology of the nanoadsorbent surface. Overall, the presented results indicate that the NEXAFS method is a

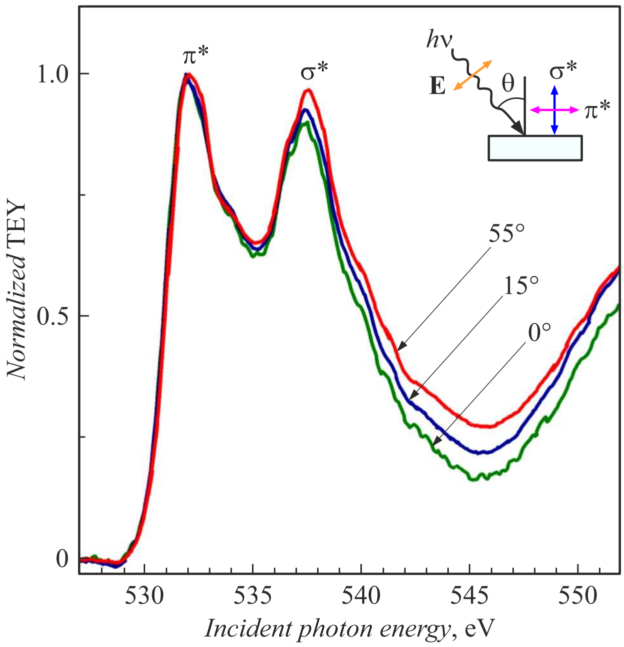

Figure 2. Normalized NEXAFS spectra for the $O_2-Yb-Si(111)$ structure at different values of angle θ. The inset illustrates the geometry of the experiment.

versatile instrument for examining the X-ray dichroism of chemisorbed molecules on both single-crystal substrates and nanofilm surfaces.

A similar conclusion regarding the orientational symmetry of O_2 molecules on the ytterbium surface may be derived from the analysis of the angular dependence of the π^* resonance in Fig. 2. When an adsorbed particle is in the vertical position, two mutually orthogonal $1\pi_g^*$ orbitals are parallel to the surface and degenerate in energy, and the angular dependences of the corresponding resonances should be identical. A different pattern is observed if the molecule is positioned horizontally. One $1\pi_g^*$ orbital is then oriented parallel to the surface ($\pi_{\|}^*$), while the other one is perpendicular to it ($\pi_{\perp}^*$). First, energy splitting is to be expected for such orbitals. Second, the resonances corresponding to them should have different dependences on angle θ. All this means that when the θ value changes, a shift in energy of the peak induced by the π^* resonance should occur in NEXAFS spectra. Such a shift was noted, e.g., in [11]. In the present study, no energy shift of the π^* resonance (peak at 532.0 eV) was observed (see Fig. 2). This is indicative of vertical orientation of O_2 molecules.

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Conflict of interest

The authors declare that they have no conflict of interest.

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