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Valence-to-core XES of Ti, TiO and TiO₂ by means of a double full-cylinder crystal von Hamos spectrometer

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Abstract

We present valence-to-core x-ray emission spectroscopy of Ti, TiO and TiO₂ by means of a double crystal von Hamos spectrometer based on full-cylinder highly-annealed pyrolytic graphite mosaic crystals. We demonstrate that, using a double crystal configuration, an energy resolution of $E/\text{E} \approx 2700$ can be achieved in a compact setup using cylindrically curved optics with a radius of curvature of 50 mm. The stated energy resolution proved to be high enough to identify and determine chemical shifts of the $K\beta_{2,5}$ and $K\beta''$ emission lines of both oxides. The experimental results are supported by calculations with the ab initio package OCEAN and compared to literature values.

Introduction

High-resolution x-ray emission spectroscopy (XES) has been proven to be an efficient experimental method for investigating the chemical environment and its effects on the electronic structure of atoms. The information gained with XES in probing occupied states is complementary to x-ray absorption techniques (XAS) [1]. For 3d transition metals the $K\beta$ emission is of particular interest. The $K\beta$ emission consists of a group of lines including the chemically not so sensitive $K\beta_{1,3}$, arising from the $1s3p$ transition, and the chemically very sensitive $K\beta_{2,5}$, arising from the $1s3d$ valence-to-core transition [2]. The 3d valence states reveal valuable information on the chemical environment. By studying the respective valence-to-core transitions conclusions can be drawn about spin structures, binding partners, oxidation states, or even bond lengths [3][4]. In literature this spectral region and the experimental method associated with investigating these spectra are widely referred to as $K\beta$ ($K\beta$ -XES) [5][6] or valence to core x-ray emission spectroscopy (vtc-XES) [7]. The emitted x-rays resulting from these transitions are in the tender to hard x-ray regime (4.0 keV to 9.5 keV) making this method less sensitive to the sample environment (ambient pressure, liquid environment).

These spectral features are characterized by chemically induced energy shifts of only a few eV and relatively low transition probabilities. Hence, they require an experimental setup characterized by a high energy resolution and discrimination capability as well as sufficient

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efficiency in order to resolve these features. Generally, these requirements are met by wavelength-dispersive spectrometers.

In this work we measured chemical shifts in the $K\beta$ emission spectrum of titanium(II) oxide (TiO) and titanium dioxide (TiO₂) with respect to metallic titanium (Ti) by means of a wavelength-dispersive spectrometer operated in the novel full-cylinder von Hamos geometry. The experiments were realized using a well-known polychromatic excitation source. Highly-annealed pyrolytic graphite (HAPG) mosaic crystals are used as dispersive elements since this type of crystal offers a high reflectivity at mosaic spreads below 0.1° [8]. We demonstrate that a sufficient spectral resolution for vtc-XES applications is achieved with a crystal curvature radius of only 50 mm by adding a second crystal to the full-cylinder spectrometer concept [9]. The von Hamos geometry is associated with a very stable energy axis allowing for a reassessment of chemical energy shifts of TiO and TiO₂ with respect to metallic Ti [5][10][11]. In particular, the relative energy of the $K\beta$ emission line for TiO could be analyzed which has not been achieved in previous works [1][10]. Moreover, the experimental results are supported by theoretical spectra calculated with the ab initio OCEAN package [12][13].

Experiment

The photon-induced XES experiments were performed on the dipole white radiation beamline in the Physikalisch-Technische Bundesanstalt laboratory at the electron storage ring BESSY II [14]. Since no monochromator is installed in this beamline, the XES data is recorded using a polychromatic excitation spectrum corresponding to the 1.3 T bending magnet attenuated by a 2 μ m thick aluminum filter. A source size of well below 100 μ m is realized by means of the beamline apertures resulting in an estimated photon flux of 10⁷ photons/s with photon energies above the Ti K absorption edge. The total collection time was 8h 33min per sample.

The emission spectra were measured with a von Hamos spectrometer based on two full-cylinder Bragg crystals. A similar design based on one crystal is described elsewhere [15]. In the used configuration a full width at half maximum of the $K\beta_{1,3}$ line of 3.9 eV in first diffraction order for the metallic titanium sample was measured. Considering the reported lifetime broadening for Ti $K\beta_{1,3}$ of 1.2 eV [16] the instrumental resolution is estimated to be about $E/\Delta E \approx 2700$. A schematic of the experimental setup is given in Figure 1. All components are housed within an ultrahigh vacuum (UHV) chamber since the use of UHV conditions increases the detection efficiency of the spectrometer. In the case of Ti $K\beta$ emission the detection efficiency is increased by over 90 % compared to ambient conditions. The spectrometer is placed at an angle of 90° with respect to the excitation beam and within the storage ring plane.

The Bragg crystals each consist of 40 μ m thick HAPG mosaic crystals [17] mounted on a Zerodur full-cylinder. The HAPG crystals in use exhibit a mosaic spread of around 0.06°. The flexibility of the material enables the realization of full-cylinder optics with a radius of only 50 mm resulting in a very compact spectrometer with an effective CCD position of

around 0.5 m from the sample for the present measurement. The effective height and width of the spectrometer is around 0.1 m.

The photon detection is realized by means of a position sensitive back-illuminated in-vacuum x-ray CCD with 2048×2048 pixels with $13.5 \mu\text{m} \times 13.5 \mu\text{m}$ pixel size. Due to the full-cylinder geometry, the CCD detects circular diffraction patterns. A polar integration results in an intensity distribution as a function of radius. The radius is then converted to photon energy by considering the Bragg-condition and the tabulated emission energy of the metal titanium $K\beta_{1,3}$ mainline as described elsewhere [15]. Other definitions of the energy scale become accessible when using scattered excitation radiation at monochromator beamlines.

All three samples were mounted on identical sample holders ensuring an incidence angle of 45° . The metallic Ti sample was purchased as a $1 \mu\text{m}$ thick, unsupported foil. The TiO and TiO₂ samples were obtained as powders with particle diameters of $40 \mu\text{m}$ and compressed to 1 mm thick specimen.

Calculation

Calculations were carried out using OCEAN [12][13]. The electronic ground state was calculated with density-functional theory within the local-density approximation using the QuantumESPRESSO code [18]. A neon-core pseudo potential was constructed for titanium using the OPIUM code [19]. For oxygen the FHI pseudo potential was used from the QuantumESPRESSO website. A plane wave cut-off of 150 Ryd. was used for the calculations. The lattice constants for each compound were taken from experiment [20]. An effective core-hole lifetime broadening of 0.19 eV was applied to the calculated spectra. For comparison purposes, the calculated emission spectra were aligned with the respective measured $K\beta_{1,3}$ lines.

Results and Discussion

The obtained $K\beta$ emission spectra are shown in Figure 2. Due to different mass depositions of the samples, all spectra were normalized to the peak intensity of the $K\beta_{1,3}$ line. This line has the highest transition probability in the spectral range recorded and originates from the 3p-1s transition in the titanium atom. The $K\beta'$ line on the low-energy shoulder results from splitting due to spin-orbit coupling [6]. This feature is not further discussed due to insufficient discrimination capability. The $K\beta_{1,3}$ lines of both titanium oxides experience a slight shift ($< 1 \text{ eV}$) to lower energies as compared to the metallic titanium. Although this is expected [6], the uncertainties in the absolute line energies are estimated to be above 1 eV. These rather large uncertainties are due to uncertainty in the effective sample position within the setup, i.e., the source position in the von Hamos spectrometer. The distance from the sample to the CCD affects the absolute energy scale of the spectra. A validation of either the sample position or energy scale after switching samples is necessary in order to determine absolute line energies with low uncertainty. Thus, in the following analysis line energies of the vtc-XES features are referenced to the respective $K\beta_{1,3}$ energy.

The vtc-XES features arise on the high-energy shoulder of the $K\beta_{1,3}$ line and are extracted for further analysis. This extraction is realized by modeling and subtracting the high-energy tail of the $K\beta_{1,3}$ line from the respective spectrum by considering data points of the $K\beta_{1,3}$ above and below the vtc-XES features [7]. A sum of a Voigt function and a third degree polynomial is used as model function. The polynomial accounts for the asymmetry of the spectrometer response function caused by the mosaicity of the Bragg crystals and the full-cylinder geometry. The modeling of the oxide spectra is adapted from the metallic Ti model and adjusted with respect to the $K\beta_{1,3}$ energy. The resulting vtc-XES data is presented in Figure 3 with an energy scale referring to the energy difference to the respective $K\beta_{1,3}$ peak centroid. Two features are identified: the $K\beta_{2,5}$ line (also referred to as $K\beta_5$ [11]) and the $K\beta''$ line representing transitions from valence bands to the 1s core hole.

The $K\beta_{2,5}$ line is present in all three spectra while the $K\beta''$ is only observed for the oxides, i.e., in the presence of a ligand atom. In addition, the emission lines for TiO are both shifted by roughly 5 eV to lower energies as compared to the other two compounds. The results obtained by the analysis of this data are summarized in Table 1 with uncertainties derived from the extraction and fit procedure. Note that the uncertainties for $K\beta''$ are higher since the peak position is more effected by the extraction from the $K\beta_{1,3}$ tailing. Calculations suggest a more complex, yet similarly distributed structure of the vtc-XES features. This reflects the complexity of the valence molecular orbitals involved in the observed transitions. To quantify the respective calculated energetic positions of these structures, however, the centroid is determined and added to Table 1.

Transition probabilities describing the relative peak intensities of the emission lines are not derived from the experimental data. The determination in this spectral region demands detailed knowledge of the energetic absorption behavior in order to account for self-absorption of the emission lines. This information could be revealed by means of transmittance measurements using tunable radiation of high spectral purity if the thickness of the samples is appropriate to allow for such an investigation. It has been shown that the near-edge x-ray absorption structure is significantly affected by the chemical binding [1] [11], thus, requiring an individual absorption correction for each species.

Conclusion

We demonstrate the capability of a compact double crystal von Hamos spectrometer based on HAPG mosaic crystals to achieve a spectral resolving power for vtc-XES analysis of Ti, TiO and TiO₂. Applying an extraction procedure from the $K\beta_{1,3}$ main line, relative energies of the $K\beta_{2,5}$ and $K\beta''$ emission lines could be determined. The experimental values and results reported elsewhere are in good agreement within the combined uncertainties for Ti and TiO₂, but the values for the $K\beta_{2,5}$ of TiO are slightly off. Furthermore, we could substantiate the existence of the $K\beta''$ emission line for TiO and support this result by means of an ab initio calculation. The calculation shows overall good agreement with the experimental results, however, deviations, especially for the oxide related $K\beta''$ emission lines, are noticeable.

Uncertainties in absolute sample position are the largest contributor to the uncertainty in the measured $K\beta_{1,3}$ lines and could be reduced in future measurements. The calculated emission spectra for the oxides yield a splitting between the $K\beta''$ and $K\beta_{2,5}$ lines that is too small compared to experiment. This is not unexpected given the propensity of density-functional theory to give electronic structure that underestimates the band widths (and band gaps) of materials [18]. Future work should incorporate more sophisticated density functionals or self-energy corrections. Furthermore, the experimental set up could benefit from an x-ray focusing optic such as a polycapillary which increases the photon flux on the sample, thus, decreasing the total collection time.

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Figure 1.

Schematic of the experimental setup in a) side view and b) front view of the CCD. The sample is excited with polychromatic x-rays in order to ionize the K-shell or 1s state of the titanium atoms. The emitted photons from the sample have to meet the Bragg condition at each HAPG crystal with radius R in order to be detected by the CCD. The spectra are obtained via polar integration over the detected circles.

Figure 2.

K β emission spectra of Ti, TiO and TiO₂ normalized to the K $\beta_{1,3}$ maximum. The fitted K $\beta_{1,3}$ high-energy tailing is only shown for the metallic TiO spectrum to illustrate the extraction of the vtc-XES data. The energy scale is referred to the metal Ti K $\beta_{1,3}$ taken from [21].

Figure 3.

Extracted vtc-XES spectra for Ti, TiO and TiO₂ in comparison to calculated emission spectra by OCEAN.

Table 1.

Experimental energy differences (exp.) of the vtc-XES peaks in comparison to calculations (calc.) and literature values.

sample	reference	E /eV		
		$K\beta_{2,5} - K\beta_{1,3}$	$K\beta'' - K\beta_{1,3}$	$K\beta_{2,5} - K\beta''$
Ti	exp.	30.7(3)	-	-
	calc.	30.4	-	-
	Koster [5]	30.9	-	-
TiO	exp.	25.3(3)	9.9(8)	15.4(10)
	calc.	25.4	12.3	13.1
	Mandic [10]	26.3(5)	not resolved	not resolved
TiO ₂	exp.	29.9(2)	14.6(6)	15.3(7)
	calc.	28.8	15.8	13.0
	Mandic [10]	29.8(5)	15.1(2)	14.7(5)
	Koster [5]	30.4	15.2	15.2