Anisotropy and Collection Angle Dependence of the Oxygen *K* ELNES in V_2O_5 : A Band-Structure Calculation Study

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Dedicated to Professor E. Zeitler on the occasion of his 75th birthday

Abstract

We present a theoretical study of the anisotropy and collection angle dependence of the oxygen *K* ELNES in V_2O_5 . *Ab-initio* band-structure calculations were performed with WIEN97, a program package based on the full potential linearized augmented plane waves (FP-LAPW) method. An analysis of the site and angular momentum projected DOS allowed the identification of differently coordinated oxygens and the separation of the oxygen *K*-edge into contributions from terminal (vanadyl) oxygens, bridging oxygens and chain oxygens. The major contribution to the anisotropy of the O *K*-edge ELNES could be assigned to transitions at the vanadyl oxygen. Theoretical calculations predict that the extent of changes in the ELNES would be large enough for detection in collection angle dependent O *K*-edge measurements. A variation in the fine structure of the O *K*-edge with decreasing collection angle was confirmed by experiments.

Keywords: Electron energy-loss spectroscopy, Band structure calculation, Density of unoccupied states, Anisotropy, Vanadium Oxides

Introduction

One of the most important applications of EELS is the analysis of the core-level energy loss near-edge structure (ELNES), which is related to the density of states (DOS) above the Fermi level. Due to the high localisation of the core level states, ELNES reflects the local DOS at the site of the excited atom. Furthermore, core-level transitions are governed by dipole selection rules and hence, the obtained ELNES corresponds to a site and angular momentum projected DOS [1]. For an anisotropic solid, the ELNES depends on the crystallographic orientation of the probed sample relative to the momentum transferred from incident to target electron. The capability of ELNES to detect the

anisotropy of the sample has previously been applied to hexagonal BN and graphite structures [2, 3]. This work is focused on the variations in the O *K* ELNES of V_2O_5 as a function of the spectrometer collection angle. We present a band-structure calculation of the anisotropy and compare simulations of collection angle dependent EELS spectra with the result of experiments. *Ab-initio* calculations were performed with WIEN97, a program package based on the full potential linearized augmented plane waves method, that allows the calculation of the angular-momentum projected DOS at the appropriate atomic site [4]. From the calculated partial DOS, the ELNES was calculated with the program TELNES [5]. We show that the site- and angular momentum projected DOS leads to a correct solid-state interpretation of

the spectral features in the oxygen K-edge and its orientation dependence.

Divanadium pentoxide represents an ideal system for the investigation of anisotropy due to its layered crystal structure. Additionally, it attracts attention due to its relevance as an ingredient to heterogeneous catalysis [6,7]. Geometric and electronic structure effects have previously been studied by Šipr *et al.* in polarized V K-edge absorption [8] and by Eyert *et al.*, who concentrated on the role of the deformation of the VO₆ octahedron on the DOS of V₂O₅ using an augmented spherical wave approach within the local density approximation [9]. Chakrabarti *et al.* studied geometric and electronic properties of the bulk as well as the (001) oriented surface of V₂O₅ using the WIEN97 code [10]. In the present work, the anisotropy of the O K-ELNES and its collection angle dependence when measured with a TEM are studied by means of band-structure calculation and spectrum simulations. We studied the O K-edge because its structure is well resolved at an energy resolution of 1 eV, whereas for the investigation of V L₃-edge fine structures an energy resolution of at least 0.2 eV is required [11]. Additionally, the O K-edge can easily be calculated by band structure methods in contrast to the V L-edge where the electrons of the probed *d*-states are more localised [12] and single particle DOS approximations fail.

Structure of V₂O₅

V₂O₅ forms an orthorhombic (P_{mmn}) layer crystal with the lattice constants $a = 1.1510$ nm, $b = 0.3563$ nm, and $c = 0.4349$ nm. The physical layers with normal direction along [001] are composed of distorted VO₆ octahedra sharing edges and corners. The structure may be considered as tetragonal pyramids: zig-zag ribbons of tetragonal pyramids share edges and form sheets by sharing corners with adjacent ribbons on both sides (Fig. 1). The weak V-O interaction between the sheets gives rise to the layered structure and an easy cleavage of V₂O₅ along (001) planes.

Fig. 1: Crystallographic structure of V₂O₅ with netplanes stacking along the c-axis. Vanadyl, chain, and bridge oxygens are shaded in light gray, gray and black, respectively. The bigger spheres correspond to vanadium atoms.

Fig. 2: Octahedral environment of the V atom in V₂O₅. The different oxygen centers are singly coordinated O(1), doubly coordinated O(2) and triply coordinated O(3).

Three different types of oxygen exist in V₂O₅ (Fig.2): the terminal (vanadyl) oxygens, O(1), which form one strong bond at a distance of only 1.58 Å, the bridging oxygens, O(2), connecting two vanadium centers at a V-O distance of 1.78 Å with a V-O(2)-V angle of 125°, and the chain oxygens, O(3), which form two bonds at 1.88 Å and one at 2.02 Å [13] with vanadium. The multiplicity is 4 for vanadium, vanadyl- and chain oxygen and 2 for the bridge oxygen.

Band structure Calculations

Band-structure calculations were performed with the WIEN97 code [4]. The core hole left by the excited electron was neglected. The number of *k*-points and the plane wave cut-off were increased until no changes were observable in the ELNES (84 *k*-points and 31 Ry respectively). Atomic sphere radii were 1.5 a.u. for vanadium, 1.4 a.u. for vanadyl oxygen O(1) and 1.8 a.u. for bridge O(2) and chain O(3) oxygen. The generalised gradient approximation was used as exchange-correlation potential [14]. The core level EELS was calculated as the sum of site and angular-momentum projected DOS and DOS-cross terms multiplied by the appropriate transition matrix elements [5]. Instrumental and excited state lifetime broadening were taken into account in the calculations.

Density of states

The diagram in Fig. 3 presents the calculated total vanadium and oxygen DOS. The Fermi level is denoted by the line at 0 eV and separates the valence band which mainly consists of O 2*p* states from the vanadium dominated conduction band. Due to the strong hybridisation between the oxygen 2*p* and vanadium 3*d* states, distinct structures in the vanadium DOS are reflected by the oxygen density of states.

Fig. 3: The total vanadium and oxygen DOS. Common structures in the DOS reflect the strong hybridisation between oxygen 2p and vanadium 3d states.

Symmetry projected DOS at the V site

An essential point for the interpretation of features in the ELNES is that spectral features related to p^* and S^* states can be distinguished because of their different energies:

Fig. 4: Vanadium 3d DOS. The vertical line indicates a change in the band character from p^* to S^* forming states.

The $3d_{xy}$, $3d_{xz}$ and $3d_{yz}$ orbitals form p type antibonds with the ligand oxygen $2p$ orbitals and appear at lower energy in the DOS (Fig. 4), whereas the $3d_{x^2-y^2}$ and $3d_{z^2-r^2}$ orbitals hybridise with the oxygen $2p$ orbitals via s like anti-

bonds mainly above 4.7 eV above the Fermi level. The splitting of $3d$ states results mainly from the cubic part of the crystal field and the strong distortion of the oxygen octahedra. The vertical line in Fig. 4 indicates the change of the dominant V $3d$ character.

Symmetry projected DOS at the O site

The figures 5a, b, and c present the angular momentum projected DOS for each of the three different oxygens in V₂O₅. Differences in the number of bonds and the bond length as well as hybridisation between vanadium and oxygen states are reflected in the DOS. Variations of the angular momen-

tum projected DOS at a specific site result mainly from the strong deformation of the VO₆ octahedron, whereas differences in the site-projected DOS arise from differences in the bonding fold and bonding length at the different sites. In particular, the O(1) $2p_x$ and $2p_y$ partial DOS in the energy range between 3 and 4.5 eV mirror the structure of the partial vanadium $3d_{xz}$ and $3d_{yz}$ DOS, respectively. Due to the short bond length of the vanadyl oxygen, this hybridisation is strong and provides the main contribution to the first peak in the O K ELNES and, as will be shown later, to its anisotropy. The partial $2p$ DOS of the two-fold bonded O(2) is mainly characterised by the $2p_x$ and $2p_y$ states which are hybridised with vanadium $3d_{x^2-y^2}$ in a S^* and with

vanadium $3d_{xy}$ states in a p^* configuration, respectively. The O(3), which is bonded to three vanadium atoms at longer bonding distances provides a relatively weak contribution to the DOS. A comparison with the vanadium $3d$ DOS reveals that the narrow split-off conduction band between 1.8 eV and 2.4 eV mainly results from a hybridisation of a V $3d_{xy}$ with an O(3) $2p_x$ orbital. A summary of overlapping oxygen $2p$ and vanadium $3d$ orbitals was given by Ewert et al [9].

Fig. 5a, b, c: Density of the unoccupied 2p states of vanadyl, bridge and chain oxygen, respectively. The three diagrams reflect differences in the chemical and geometric surrounding of the different oxygens in V₂O₅.

ELNES Simulations

In EELS experiments, the recorded spectrum corresponds to an integration of the energy loss over all scattering angles from $q = 0$ up to a maximal angle, the collection angle, which is determined by the geometric mean of the beam convergence angle α and the spectrometer acceptance angle β . An important prerequisite for the detection of anisotropy by variation of the spectrometer collection angle is that the achievable angles are of comparable size in view of the characteristic scattering angle q_E . For the oxygen K-edge at $E \gg 530 \text{ eV}$ at an incident beam energy of 200 keV , the relativistically corrected characteristic scattering angle is $q_E = 1.54 \text{ mrad}$ [1]. The program TELNES accounts both for orientation and anisotropy of the specimen and for integration over collection and convergence angles in the experiment [5]. Calculations were performed for a range of collection angles in the vicinity of q_E :

The case of $\alpha = \beta = 0 \text{ mrad}$ corresponds to forward scattering. This set-up cannot be obtained in an electron microscope but would correspond to an X-ray absorption experiment with linearly polarised light. It defines the highest possible sensitivity for anisotropic effects and allows a clear splitting of the ELNES into contributions arising from excitations into differently oriented final states.

Simulations for $\alpha = 1.5 \text{ mrad}$ and $\beta = 1.4 \text{ mrad}$, 4.1 mrad and 9.8 mrad correspond, respectively, to a maximal angle between transferred momentum $\vec{q}$ and crystal c -axis of 62° , 75° and 82° . In the following, the cases of $\alpha = \beta = 0 \text{ mrad}$, $\alpha = 1.5 \text{ mrad}$, $\beta = 4.1 \text{ mrad}$ and $\alpha = 1.5 \text{ mrad}$, $\beta = 9.8 \text{ mrad}$ are discussed in more detail.

Scattering angle $q = 0$

The diagrams in Fig. 6 present the calculated O-K ELNES for the case of a momentum transfer $\vec{q}$ parallel to the principal crystallographic axis a , b and c , respectively. In each diagram, the O K-edge is split into the contributions arising from each of the different oxygens. The calculation reveals the strong anisotropy of the O-K ELNES. Differences in the local DOS are reflected in the intensities of the single contributions and underline the role of the vanadyl oxygen, which has only one strong bond of short distance with the vanadium atom.

In case of $\vec{q} \parallel a$ (Fig. 6a), transitions of O $1s$ electrons into O $2p_x$ orbitals are monitored. Two features are clearly distinguishable in the oxygen K-edge. The strong peak at lower energy corresponds to p^* final states formed by the O(1) $2p_x$ with V $3d_{xz}$ - and from a hybridisation of O(3) $2p_x$ with $3d_{xy}$ states of the two V to which O(3) is bonded at a distance of $1.88 \text{ \AA}$, respectively. The shoulder corresponding to transitions into s^* states is due to hybridisation of O(2) $2p_x$ states with V $3d_{x^2-y^2}$ and O(3) $2p_x$ with

Fig. 6a, b, c: O K-edge simulated for forward scattering conditions. The direction of the transferred momentum lies parallel to the a , b and c direction, respectively. In each diagram contributions of the three different oxygens weighted by the number of atoms in the unit cell are shown.

the $3d_{x^2-y^2}$ of the V atom to which O(3) is bonded at a .

For $\vec{q} \parallel b$ (Fig. 6b), transitions of O $1s$ electrons into O $2p_y$ orbitals are selected. In case of O(1) and O(2), the final states are hybridised with V $3d_{yz}$ and $3d_{xy}$, respectively. Their contributions cause the main peak at about 4 eV . The final $2p_y$ state of the O(3) hybridises with V $3d_{xy}$ and with

$V 3d_{x^2-y^2}$, where the latter causes the slight shoulder at about 5 eV.

For $\vec{q} \parallel c$ (Fig. 6c), transitions of O 1s electrons into O $2p_z$ orbitals are selected. The resulting oxygen K-edge consists mainly of a peak at about 6 eV and is dominated by transitions at the O(1). The peak results from a S^* overlap of a final O(1) $2p_z$ state with a $V 3d_{z^2-y^2}$ state. O(2) contributes with transitions to states hybridised with $V 3d_{xz}$ and O(3) contributes with transitions into $2p_z - 3d_{xz}$ and $2p_z - 3d_{yz}$ hybrids.

The cases where the transferred momentum lies either parallel to the *a* or *b* axis demonstrate that the in-plane anisotropy causes the O(2) to interact with vanadium via S^* in the *a* direction and via p^* along *b*. Contributions from O(3) suggest that along *a* the p^* interaction O $2p_x - V 3d_{xy}$ is stronger, whereas in the *b* direction the S^* interaction (O $2p_y - V 3d_{xy}$) seems to be enhanced. To one point this might be a result of the smaller distance between vanadium and the O(3) atoms along the *b* direction. Another point is the fact that O(3) $2p_y$ orbitals find two vanadium partners for a S^* interaction and only one for a p^* interaction whereas the case is turned around for the p_x orbitals which can form two p^* and only one S^* combination with adjacent vanadium atoms.

Finite collection angle

The diagrams in Fig. 7 – Fig. 8 present the calculated O-K ELNES for collection angles of $b = 4.1$ mrad and 9.8 mrad, respectively. The collection angle dependence of the O K-edge becomes apparent.

At $b = 4.1$ mrad additional contributions due to transitions into final states within the plane perpendicular to the direction of the incident beam modify the shape of the edge. In fact, each of the spectra presented in Fig. 7 is a composition of the spectra observed for forward scattering along each axis. As a result, the anisotropy within the *ab*-plane is nearly averaged out at $b = 4.1$ mrad and the O-K ELNES looks similar if the electron beam coincides with either the *a*- or the *b*-direction, albeit the individual contributions of O(1) and O(2) differ.

For an incident beam parallel to the *c*-axis, contributions from transitions into final p^* states mainly at the O(1) and O(2) cause an alteration of the intensities of the p^* and S^* features (Fig. 7c).

At a collection angle of $b = 9.8$ mrad (Fig. 8) the anisotropy of the ELNES is already averaged out and the calculated oxygen K-ELNES along the three zone axis are exactly similar. Thus, the calculations predict a strong collection angle dependence for the oxygen K-ELNES in V_2O_5 if the

spectrum is recorded in an orientation where the crystal *c*-axis coincides with the direction of the incident electron

Fig. 7a, b, c: O K-edge simulated for $a = 1.5$ mrad and $b = 1.4$ mrad. For each direction the contributions of the three different oxygens are shown, weighted by the number of atoms in the unit cell.

beam. On the other hand, only a weak collection angle dependence can be expected if the incident beam lies parallel to the *b*-axis, and nearly no variations may be detected in measurements where the electron beam lies parallel to the *a*-axis. This reflects the anisotropy in the local surroundings of the different oxygen atoms in V_2O_5 and of the crystal itself.

The anisotropy is smaller within the *ab*-plane than within any plane containing the *c*-axis.

Fig. 8: O K-edge simulated for $a = 1.5$ mrad and $b = 9.8$ mrad. The direction of the incident electron beam does not have an effect on the ELNES anymore: all effects of anisotropy are averaged out.

Comparison to experiment

Measurements were performed on V_2O_5 single crystals of uniform thickness in [001] orientation (coincidence of the crystal *c*-axis with the direction of the incident electron beam). All spectra were recorded with a Gatan energy filter on a Philips CM200 FEG microscope, operated at 200 kV. The collection angles were determined by the objective aperture in the image mode (9.4 mrad and 4.1 mrad) and by the camera length and spectrometer entrance aperture in diffraction mode (1.4 mrad and 0.68 mrad). The spectra were acquired at a convergence angle of $a = 1.5$ mrad. The acquisition time was kept reasonably small (5 to 10 seconds) and diffraction patterns were recorded after each measurement in order to prevent errors due to electron beam induced reduction of the sample. Figure 9 displays the experimental data of the oxygen K ELNES, recorded in the *c*-direction after background subtraction and deconvolution for multiple scattering corrections [1]. The trailing edge of the V L_2 white line is superimposed on the oxygen K edge in the spectra. Due to the fact that the V L -edges can not be simulated within a one particle approximation, the falling slope of the L_2 post edge region was removed from the spectra by fitting the L_2 and L_3 edges with an admixture of a Gauss- and Lorentzian function. Although this routine is only a rough approximation, the recovered O K-edge is more realistic than that without removal of contributions from the L_2 -edge. Figure 10 presents the simulated ELNES, gained for the same settings of *a* and *b*. The experimental results confirm the collection angle dependence of the oxygen K ELNES and hence, the anisotropy described above.

All the features of the O K-edge are well reproduced by the simulation. Moreover, the changes in the S^*/p^* ratio with increasing collection angle are identical in simulation and experiment. The p^* peak is systematically slightly underestimated in the simulation. This is probably a consequence of the effect of the core hole left by the excited elec-

tron. The fact that the final state is an excited state was not taken into account since WIEN97 only allows ground-state calculations. A more convincing agreement may be achieved by inclusion of a local approximation of the core hole effect by a Z+1 approximation. It has been observed previously on an insulator that the effect of the core hole tends to be an increase of the structures situated at the edge onset [15].

Fig. 9: ELNES recorded with incident beam parallel to the crystal *c* direction at different collection angles after background subtraction and removal of plural scattering. The preceding V L_2 edge was removed by fitting an admixture of a Gauss- and Lorentzfunction to the V L_2 and L_3 edges.

Fig. 10: ELNES simulated for an incident beam parallel to the crystal *c*-axis.

Summary

The anisotropy and collection angle dependence of the O-K ELNES in V_2O_5 was studied theoretically by means of ab-initio band structure calculations. The site and angular-momentum projected DOS allows a detailed discussion of the orbital hybridisation between oxygen 2*p* and vanadium 3*d* states. The anisotropy in bonding fold and the strong deformation of the VO_6 octahedra results in variations of the partial DOS. This is reflected by the ELNES which is uniquely determined by the type of interaction (p^* or S^*) between oxygen 2*p* final states and vanadium 3*d* states. The unoccupied 2*p* DOS of the O(3) is quite diffuse and, compared to the O(1) and O(2) 2*p* DOS, relatively weak. Therefore, the effect of structural anisotropy on the O(3) ELNES

is minuscule. The partial $2p_x$ and $2p_y$ DOS of O(1) are quite similar and hence, O(1) does not evoke any anisotropy within the *ab*-plane. The main contribution to anisotropy within the *ab*-plane arises from transitions at O(2).

But, similar to the case of O(3), the contribution to anisotropy caused by O(2) is small and thus, might not be detected with EELS.

The calculations show that major changes in the fine structure arise when the direction of the transferred momentum $\vec{q}$ leaves the *ab*-plane and additional contributions from transitions into final states perpendicular to the *ab*-plane are recorded. Changes to the fine structure originate from the anisotropy of the O(1) $2p$ DOS within any plane containing the *c* axis and are very well detectable as confirmed by the

experiment. Our results reveal a collection angle dependent detectability of anisotropy in the ELNES: for V₂O₅, the anisotropy in the O K-edge is already averaged out and spectra collected along the three zone axis coincide at a collection angle of 9.8 mrad, which is, on the other hand, a magnitude reasonable for gaining a sufficient signal for EELS recording.

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