Electronic structure of VO$_2$ studied by x-ray photoelectron and x-ray emission spectroscopies

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Abstract. A VO$_2$ single-crystal has been subject of a combined investigation by high resolution x-ray photoelectron spectroscopy (XPS), x-ray emission spectroscopy (XES) with both electron and energy-selective x-ray excitation (V Lα-, V Kβ$_5$- and O Kα-emission) and x-ray absorption spectroscopy (XAS) (O1s). We performed first principles tight-binding LMTO band structure calculations of VO$_2$ in both monoclinic and tetragonal rutile structures and compare the densities of states (DOS) with the experimental data. From this we conclude that the electronic structure of VO$_2$ is more bandlike than correlated.

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1. Introduction

VO$_2$ belongs to transition metal compounds which exhibit metal-insulator transitions \[1\]. At $T = 340$ K, VO$_2$ undergoes a phase transition from a semiconductor with monoclinic structure to a metal with the tetragonal rutile structure. The nature of the ground-state semiconducting phase is still rather uncertain. In the semiconducting phase, the V atoms are paired which was a reason for the suggestion that the electron-phonon interaction is responsible for the splitting of the $d$-band and the opening of a band gap \[2\]. This idea is supported by band structure calculations according to which the crystallographic phase transition can be explained by the formation of a charge-density wave accompanied by a lattice distortion and a subsequent condensation of phonons \[3\]. According to Ref. \[4\], there is enough energy gain to account for the metal-insulator transition through structural distortions that permits a strengthening of the vanadium $d$–$d$ bonds and a reorganization of the states near the Fermi level.

On the other hand, some calculations indicate that a crystallographic distortion is not sufficient to open up a gap, and that the electron-correlation effects play an important role in the transition \[5\]. It was concluded in Ref. \[6\] that the energy gap in VO$_2$ is of the charge-transfer type rather than of the Mott–Hubbard type as in the late transition metal compounds, like NiO and CuO \[7\].

In addition to earlier spectroscopic studies \[8, 9, 10, 11\], the photoelectron spectroscopy measurements and low-energy electron diffraction studies on VO$_2$ have been carried out recently in Ref. \[12, 13\]. The present work aims at a combined experimental study of the electronic structure of a VO$_2$ single crystal at room temperature by the use of high-energy spectroscopies. A high-resolution x-ray photoelectron spectroscopy (XPS) provides information about the total density of states (DOS) in the valence band (VB); V$L$\textsubscript{α} (the $3d4s \rightarrow 2p$ transition), V$K$\textsubscript{β}$_5$ (the $4p \rightarrow 1s$ transition), O$K$\textsubscript{α} (the $2p \rightarrow 1s$ transition) x-ray emission (XES) VB spectra (excited by both electrons and photons) probe the V$3d$, V$4p$ and O$2p$ partial DOS in the valence band; the O$1s$ total electron yield spectrum probes the O$2p$ unoccupied states. Band structure calculations are performed and compared with the experimental spectra leading to the conclusion that the electronic structure of VO$_2$ is more bandlike than correlated.

2. Experimental procedure

The XPS measurements have been carried out with a PHI 5600 ci multitechnique spectrometer using monochromatized aluminium $K\alpha$ radiation with a full width at half-maximum (FWHM) of 0.3 eV. The energy resolution of the analyzer was 1.5% of the pass energy. We estimate an energy resolution of about 0.35 eV for the XPS measurements on VO$_2$. The base pressure in the vacuum chamber during the measurements was $5 \times 10^{-9}$ Torr. All of the experiments presented in this paper have been performed at room temperature with the same single crystal of VO$_2$ (2 × 7 × 0.5 mm).

Initial measurements were performed without cleaving the crystal, and hence a high contamination of carbon was detected on the surface. Therefore the final measurements were done on a surface that was cleaved \textit{in vacuo}. Thus an excellent surface with a relatively small amount of defects and contaminations could be obtained, and hence the intrinsic properties of the samples could be studied. For the comparison, XPS measurements of pure V metal (single crystal) were also performed.
All XPS spectra were calibrated using the Au 4f7/2 signal from an Au foil \(E_{b,e.}(4f7/2) = 84.0 \text{ eV}\).

Electron excited VLo-emission spectra (the 3d4s \(\rightarrow 2p3/2\) transition) of VO$_2$ were recorded using a RSM-500 spectrometer with a diffraction grating \((N=600 \text{ lines/mm}; \ R=6 \text{ m})\). The accelerating voltage and current on the x-ray tube were \(V=4.4 \text{ keV}\) and \(I=0.3 \text{ mA}\). The energy resolution was 0.4 eV.

VK$\beta_5$-spectra (the 4p \(\rightarrow 1s\) transition) of VO$_2$ were measured using a fluorescent Johan-type vacuum spectrometer with a position-sensitive detector [4]. CuK$\alpha$ x-ray radiation from the sealed x-ray tube was used for excitation for the fluorescent VK$\beta_5$ XES. A quartz crystal (rhombohedral plane, second order reflection) curved to \(R=1.8 \text{ m}\) was used as an analyzer. The spectra were measured with an energy resolution $\Delta E=0.22 \text{ eV}$.

Energy-selective excited OKo- (the 2p \(\rightarrow 1s\) transition), VLo-spectra (the 3d4s \(\rightarrow 2p3/2\) transition) were measured as well as x-ray absorption spectra (the V2p- and O1s-edges) in the sample drain-current mode. These measurements were performed at the undulator beam line BW3 at HASYLAB Hamburg, Germany [1], equipped with a modified SX-700 monochromator. The soft x-ray emission spectra were recorded at various excitation energies in the first order of diffraction with a resolution of about 0.7 eV. We used a grazing-incidence grating spectrometer [16] with an \(R=5 \text{ m}\) spherical grating with 1200 lines/mm in a Rowland circle geometry. The resolution of the excitation radiation was set to about 1 eV by opening the exit slit of the monochromator to 400 $\mu\text{m}$. The spectrometer had solid angle acceptance of about $2 \times 10^{-5}$ sr, so that with a spot size of some 500 $\times$ 500 $\mu\text{m}$ at a distance of 5 cm from the entrance slit of the spectrometer we registered a maximum of about 300 counts/minute in the VLa line at 100 mA ring current. In order to obtain a reasonable statistical accuracy, we had to acquire for 120 to 240 minutes per single spectrum, depending on the excitation energy. The angle between the incident x-ray beam and the detection direction was 90°. This minimized the elastic scattering into the spectrometer, because the polarization of the beam coincided with the detection direction. The V2p and O1s absorption spectra had energy resolution of 0.2 eV for an exit slit width of 80 $\mu\text{m}$. No special surface preparation was undertaken for these measurements.

3. Results and Discussion

3.1. Electronic Structure Calculations

The band-structure calculations were carried out by the tight-binding linear muffin-tin orbital method (TB-LMTO) in the atomic sphere approximation (ASA) [17], with the use of the exchange-correlation potential as parametrized by von Barth and Hedin [8] and gradient corrections as proposed by Langreth and Mehl [9] on top of the local density approximation (LDA). Since both rutile and monoclinic structures of VO$_2$ are relatively loosely packed, it was necessary to include empty spheres in the ASA calculations. For the tetragonal rutile phase, we used the crystal structure parameters \(a=4.5546\ \text{Å},\ c/a=0.626\) and \(u=0.300\) as given in Ref. [20]. Besides two formula units of VO$_2$, our unit cell included eight equivalent empty spheres, which form long chains parallel to the linear O-V-O fragments, separating the latter. Due to the difference between the V and O atomic sphere radii, the chains are slightly bent. Our choice of the sphere radii $S$, based on the attainability of good matching
between the potential at the V and O atomic spheres compatible with a radial sphere overlap below 25% of all interatomic distances, was: \( S(V) = 2.702 \text{ a.u.}; \) \( S(O) = 1.762 \text{ a.u.}; \) \( S(\text{empty spheres}) = 1.619 \text{ a.u.} \) The calculated band structure and the total DOS are rather close to those obtained earlier in Ref. [3, 21, 22] by different methods. We performed our own calculation because no data on the partial DOS, that are necessary for the discussion of the XES, were available from the previous calculations. Our calculated total DOS for the rutile phase of VO\(_2\) is shown in Fig. 1, upper panel.

As is usual in oxides, the valence band is formed by hybridized transition metal 3\(d\) and O2\(p\) states. The band gap of 0.9 eV within the valence band separates the regions where O2\(p\) states (below the gap) and V3\(d\) states (above the gap) dominate. The Fermi level crosses the upper subband, revealing a metallic behaviour of VO\(_2\), as consistent with the results of other calculations done for the rutile-type structure [3, 4, 21, 22]. The O2s-related subband (which experiences some hybridization with the V3\(d\) and V4\(p\) states) lies separately at about 20 eV below the Fermi level. The overall shape of the band structure and of the total DOS obtained in our calculation is in
agreement with earlier results [3, 21, 22]; the width of the gap within the valence band is somewhat larger than 0.62 eV as obtained in the full potential linear augmented plane wave calculation of Ref. [22]. The gap width of 4.6 eV reported in Ref. [3] seems to be too large (probably due to the use of the Slater exchange potential) and not in agreement with the experimental positioning of individual subbands, as discussed in Ref. [21] or found in the present paper.

Since the room-temperature phase (for \( T < 68^\circ C \)) of VO\(_2\) is monoclinic, the relevant comparison with experiment needs the calculation data for the latter structure. The monoclinic unit cell contains four formula units of VO\(_2\), and, because of the large number of atoms and low symmetry, only few calculations have been done by now. An earlier non-self-consistent calculation [23] reproduces an experimentally observable semiconductor band gap, but otherwise seems to be very inaccurate in describing the overall structure of the valence band. The analysis of the structure transformation by means of \textit{ab initio} molecular dynamics in Ref. [4] shows that the monoclinic phase has lower energy than the rutile phase, and the equilibrium positions of the atoms are in good agreement with the experimental determination. However, the strength of the tendency for opening a gap within the valence band is underestimated within the LDA, and the flat bands in the vicinity of the Fermi level do not separate completely (see, e.g., Fig. 3 of Ref. [4]). This is also the case in our calculation, which we have carried out for the experimental monoclinic structure as specified in Ref. [24].

The change from rutile to monoclinic structure gives rise to a broadening of O2\(_p\) and V3\(_d\) bands by \( \sim 0.2 \) eV and to more pronounced splitting in the V3\(_d\) states of \( t_{2g} \) symmetry. In Ref. [25] it was shown that the inclusion of electron-phonon interaction (in the periodic shell model, based on the results of discrete-variational X\(_\alpha\) cluster calculation) leads to the opening of the band gap. According to our calculation, the distortion of the nested bands due to the displacement of the atoms in the doubled-cell monoclinic structure gives rise to only small changes in the partial DOS, as compared to the rutile structure. Technically, the calculation deals with two inequivalent oxygen species and three inequivalent types of lattice-packing empty spheres of different sizes making a total of 24 sites. Our calculated total DOS for the monoclinic structure is shown in Fig. 1, lower panel, and some partial DOS are shown in Fig. 2. For comparison with XES, we did not distinguish the data for two oxygen species and show the averaged O2\(_s\) and O2\(_p\) DOS over all sites in Fig. 2, lowest panel. The densities of states are plotted for the \( 16 \times 16 \times 16 \) mesh over the Brillouin zone.

### 3.2. \textit{X-ray Photoelectron Spectra}

The intensity distribution of the VB XPS spectra reflects the total DOS of the VB, up to the deviations due to different atomic photoionization cross-sections. The results of the XPS measurements of single crystal VO\(_2\) are shown in Fig. 1 and in the Table 1.

The spectral measurements on the uncleaved crystal show a large contamination with carbon. This leads to a smearing of the fine structure in the entire valence band, a broadening of subbands and the appearance of an additional subband around 12–14 eV which we attribute to transitions from C2s states.

In the XPS spectra of the cleaved VO\(_2\) crystal, a distinct narrow peak is observed around 1 eV below the Fermi level, which, according to the results of our band structure calculations (see Fig. 3), has V3\(_d\) character. The FWHM of this peak is about 1 eV which is less than obtained in Ref. [5, 6, 10, 11].
The next subband has a two-peak structure at 3–9 eV below the Fermi level which are mainly due to the O2p states (cf. Fig. 2). Another reason for reaching this conclusion is that the energy difference between the centre of gravity of this band and the next one (located at 22 eV) is about 15 eV, which is in good agreement with the energy separation between O2p and O2s bands found in all vanadium oxides [26]. However, with the O2p and V3d atomic photoionization cross-sections for AlKα excitation [27] have a ratio of about 1:2, one may expect some contribution of V3d states in this band. This is also confirmed by our band structure calculation and by the results from the V Lα-emission measurements (see below). We point out, however, that there is a contradiction between the XPS and the ultraviolet photoelectron spectra (UPS) of VO2 given in Refs. [8, 9, 10, 11, 12, 13] with respect to energy resolution and the intensity ratio of the two peaks. The peaks are well-resolved in our measurements,
Figure 3. XPS VB spectrum of uncleaved (1) and cleaved (2) surface of VO$_2$ single crystal.

Table 1. XPS binding energies and width of the core levels (bands) of VO$_2$.

| Core level (band) | Binding Energy (eV) | FWHM (eV) |
|------------------|---------------------|-----------|
| V2s              | 630.02              | 6.10      |
| O1s              | 529.75              | 1.30      |
| V2P$_{1/2}$      | 523.48              | 2.56      |
| V2P$_{3/2}$      | 515.95              | 2.04      |
| V3s              | 68.95               | 4.54      |
| V3p              | 40.53               | 4.24      |
| O2s              | 21.73               | 2.5       |
| O2p              | 5.34; 7.24          |           |
| V3d              | 1.03                |           |

and both their energy separation and the intensity ratio are in good agreement with results of our band structure calculations.

According to Ref. [28], charge-transfer satellites are found in the UPS of ScF$_3$, TiO$_2$ and V$_2$O$_5$ in the region from 11 to 17 eV below the top of the valence band. From the resonant photoemission measurements it was concluded that the charge-transfer-type configuration manifests itself in such a way as to form a valence state in the ground state in addition to the originally filled 2$p$ state ligand. On the basis of this experimental evidence, cluster calculations of the valence photoemission and Bremsstrahlung isochromat spectra of VO$_2$ were performed in Ref. [8], and it was concluded that VO$_2$ belongs to the group of charge-transfer insulators. However, we point out that our XPS measurements of the uncleaved and cleaved VO$_2$ single crystal (Fig. 3) strongly suggest that the appearance of this structure (14-15 eV below the Fermi level) is connected with carbon contamination and that its origin is C2s states.
A similar problem was discussed in Ref. \[29\] in connection with the analysis of UPS spectra of superconducting cuprates. There, it was concluded that the satellites with binding energies of about 10 eV are generically connected with contaminations of light elements and disappear after cleaning. Therefore we have found a clear indication that the structure in question is not an intrinsic feature of the electronic structure of pure VO\(_2\) and cannot be considered as an evidence of correlation effects in VO\(_2\).

![Figure 4](image)

Figure 4. XPS O1\(_s\), V2\(_{p1/2,1/2}\) (upper panel) and V3\(_s\), V3\(_p\) (lower panel) core level spectra of VO\(_2\) and metal V.

The XPS core level spectra of VO\(_2\) are shown in Fig. 4. The energy positions of the O1\(_s\), V2\(_p\) and V3\(_p\) spectra of VO\(_2\) are close to those of Ref. \[9\], but the FWHM’s of the lines in these spectra (see Table 1) are much smaller than it was found in Refs. \[8, 9\]. The lineshapes are clearly asymmetric due to a structure seen at the high-binding energy side. In case of 2\(_p\) and 3\(_p\) levels this may be related to np\(^5d\(^1\) multiplets, as was shown in Ref. \[10\] for the V3\(_p\) spectrum. It should be noted, however, that in our measurements the V3\(_p\) lineshape is somewhat different from that obtained in Ref. \[11\].
In case of V3s level, the additional structure may be due to the exchange interaction of a (spin-up or spin-down) 3s electron left in the final state with the (V3d) electrons in the valence band.

In Fig. 4, the V2p, V3s and V3p XPS core level spectra of VO2 are compared with those of pure vanadium metal. Evidently, there is a chemical shift of the core level spectra of VO2 with respect to that of pure metal not only for the V2p XPS-line, but also for the V3s and V3p XPS-lines. The fact that the formal charge of the vanadium atom affects V3s and V3p lines in an uniform way can be used for an estimation of the oxidation state of the V atom in compounds. Recently, the same conclusion was found for the Mn3s XPS-spectra of manganese complexes in Ref. [31].

Earlier, we have shown that the analysis of 3s XPS-spectra can be used to draw conclusions about the electronic structure of 3d metal oxides [12]. It has been found that 3s XPS-spectra of NiO have a very complicated fine structure due to charge-transfer processes. In this case, an electron may be transferred from the ligand to a metal 3d-level after the emission process, and both states, the screened and unscreened one, are visible in the 3s spectrum. The simpler fine structure of the V3s XPS-spectrum in VO2 can be considered as an evidence for negligible charge transfer, again indicating that the electronic structure of this compound is more bandlike than correlated.

3.3. X-ray Emission Spectra

X-ray emission valence spectra result from electron transitions between the valence-band and a core hole. Since the wave function of a core electron is strongly localized and its angular momentum symmetry is well defined, these spectra reflect the site-projected and symmetry-restricted (in accordance with the dipole selection rules) partial DOS. In the case of VO2, we have investigated VLYα- (3d4s → 2p3/2 transition), VKβ5- (4p → 1s transition) and OKα-emission spectra (2p → 1s transition) which reflect the distribution of V3d4s, V4p and O2p partial DOS. By XPS we can measure the binding energies of the V2p and the O1s core levels so that we can determine the position of the Fermi level in the X-ray emission spectra.

The OKα and VLYα spectra, adjusted in such a way as to have a a common energy scale with the X-ray photoemission spectrum, are shown in Fig. 5. The VKβ5 spectrum is positioned with respect to XPS by matching the position of the peak which results from the hybridization with O2s states. In the same figure, the partial DOS as calculated for the monoclinic phase and broadened with an energy-dependent lorentzian linewidth according to Ref. [33] are shown. Calculated and broadened partial DOS have been rigidly shifted with respect to the Fermi energy (arbitrarily, but by the same value for all spectra) to account for a systematic error in the energy matching of the measured spectra and calculated DOS due to, e.g., the absence of the band gap in the calculation.

As is seen, the main maximum of the OKα spectrum (O2p states) is placed near the top of the valence band, that is quite common in oxides, and is essentially nonbonding. A corresponding feature is also seen in the XPS but merely as a shoulder at 4 eV, due to a smaller value of O2p photoionization cross section as compared to V3d [12]. XPS VB fine structure with two peaks at 5.4 and 7.5 eV reveals the O2p–V3d bonding band, which overlaps in energy with the maximum of the VLYα spectrum and with a high-binding energy hump of the OKα spectrum.

We have excited OKα emission at two excitation energies (E=530.8 and 532.2
Figure 5. Dots: The comparison of XPS VB, XES (OKα (fluorescent excitation at $E=530.8$ eV), VLα (curve 1 corresponds to electron excitation at $E=4.4$ keV, curve 2 - to fluorescent excitation at $E=519.0$ eV), VKβ5 (fluorescent excitation at $E=15$ keV)) and XAS O1s spectra of the VO2 single crystal. Dashed lines: broadened partial O2p, V3d and V4p (from top to bottom) DOS as calculated for monoclinic VO2.

eV) which correspond to the maxima of O1s x-ray absorption spectrum (XAS), but found only little difference. The VLα-emission spectrum has been obtained with both electron and photon excitation, that resulted in different intensity distributions (curves 1 and 2 in Fig. 5). With electron excitation at $E=4.4$ keV (curve 1), we have simultaneous excitation of VLα ($3d4s \rightarrow 2p_{3/2}$) and VLβ-emission ($3d4s \rightarrow 2p_{1/2}$) which are separated by only 7.53 eV. Therefore there is an overlap of the high-energy subband of VLα XES with the main peak of the VLβ-emission spectrum. For an excitation energy $E=519.0$ eV (curve 2), we selectively excite VLα which follows electron transitions from the occupied part of the V3d band. From these data one can conclude that there is a considerable admixture of V3d states in the O2p-like bands, so that the maximum emission comes from the V3d–O2p hybridized band and not from an only slightly populated V3d band. We find that the fine structure and energy position of the subbands of the VLα-emission spectrum are in reasonable agreement.
with the calculated V3\textit{d} partial DOS distribution given in Fig. 2.

The \( VK\beta_5 \)-emission spectrum has two main subbands whose energy positions are very close to the O2\( p \) and the O2\( s \) bands due to V4\( p \)-O2\( p \) and V4\( p \)-O2\( s \) hybridization (see Fig. 2). The splitting of the main subband of the \( VK\beta_5 \)-emission spectrum also follows the calculated V4\( p \) DOS distribution in this energy region. It is seen that the admixture of the V4\( p \) states to the V3\( d \) band is too small to be detected in the \( VK\beta_5 \) XES of VO\(_2\). The disagreement by \( \sim 2 \) eV between spectra (XPS; \( VK\beta_5 \)) and calculated DOS in what regards the position of the O2\( s \) states is known in oxides. It is related to the fact that the hole relaxation, which effectively increases the binding energy of an electron leaving a comparatively localized state such as O2\( s \), is not taken into account in our band structure calculations which describe the ground state but not excitations.

It should be mentioned that soft x-ray fluorescence spectra of VO\(_2\) (\( VL\alpha \), \( V\beta \), \( OK\alpha \) XES) were also recently reported in Ref. [11] and are compared with an UPS spectrum (measured at \( E = 501.1 \) eV): however, no XPS measurements of the V2\( p \) and the O1\( s \) binding energies are included there. The \( OK\alpha \) XES of Ref. [11] does not show the two-peak structure found in our measurements.

### 3.4. Total-electron-yield Spectra

O1\( s \) XAS of VO\(_2\) probes the O2\( p \) unoccupied states. Such spectra, with good energy resolution, have been published earlier, by Abbate \textit{et al.} [34]. In order to compare the XES obtained on the same samples which were used in the XPS, we include in Fig. 2 our own O1\( s \) spectrum obtained (for the monoclinic phase) in the sample drain-current mode. The Fermi level has been determined with the help of the XPS binding energy of the O1\( s \) level given in table 1. The O1\( s \) spectrum was measured in a rather restricted energy range, so that we can only compare the spectra in the vicinity of the Fermi level.

The fine structure of the O1\( s \) spectrum is in agreement with the shape of the O2\( p \) conduction band in our electronic structure calculations (Fig. 2). In the high-temperature rutile phase, the calculated conduction band exhibits a pronounced two-peak structure, also discussed in Ref. [34]. In the low-temperature monoclinic phase, a further splitting of the conduction band is seen from the calculations, in agreement with a more pronounced structure in the O1\( s \) spectrum of Ref. [34].

### 4. Conclusion

The results of measurements of high-resolution x-ray photoelectron spectra, \( VL\alpha \), \( VK\beta_5 \) and \( OK\alpha \) x-ray emission spectra (obtained by using both electron and x-ray excitation) and O1\( s \)-absorption spectra of a VO\(_2\) single crystal are presented. They are compared with first-principles LMTO band structure calculations of VO\(_2\) in monoclinic and tetragonal rutile phases. It is concluded that the electronic structure of VO\(_2\) is more bandlike than correlated.

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