

# Direct Imaging of Octahedral Distortion in a Complex Molybdenum Vanadium Mixed Oxide

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Dedication ((optional))

**Abstract:** Complex Mo, V based mixed oxides that crystallize in the orthorhombic M1-type structure are promising candidates for the selective oxidation of small alkanes. The oxygen sub-lattice of such a complex oxide has been studied by annular bright field scanning transmission electron microscopy. The recorded micrographs directly display the local distortion in the metal oxygen octahedra. From the degree of distortion we are able to draw conclusions about the distribution of oxidation states in the cation columns at different sites. The results are supported by X-ray diffraction and electron paramagnetic resonance measurements that provide integral details about the crystal structure and spin coupling, respectively.

In the past 25 years, high resolution transmission electron microscopy (HRTEM) has been developed to a powerful tool for direct imaging of atomic structures.<sup>[1]</sup> However, direct imaging of elements with low atomic number, such as oxygen, nitrogen or hydrogen is difficult due to their low scattering power. For instance, in high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) intensity is due to Rutherford scattering by the nuclei and, therefore, approximately proportional to  $Z^2$ .<sup>[2]</sup> As a result the intensity of heavy elements generally overwhelms the signal of light ones. Nonetheless, individual oxygen columns have been observed by advanced techniques, such as exit wave reconstruction,<sup>[3]</sup> spherical aberration corrected TEM,<sup>[4]</sup> or high voltage HRTEM.<sup>[5]</sup> Although these methods show concepts to pinpoint the oxygen columns, their utilization is limited.

Pioneering work on direct imaging of oxygen columns was mainly accomplished on structures derived from

thermodynamically stable, high-temperature perovskites characterized by negligible beam sensitivity.<sup>[4b, 5]</sup> In catalysis and energy conversion, however, metastable and specifically beam sensitive phases exhibiting defects and distortions in the metal-oxygen polyhedra are generally used. Direct imaging of light elements in beam sensitive materials is, however, possible by using an annular bright field (ABF) - detector<sup>[6]</sup> in combination with STEM. Small angle scattering occurs at the edge of the atoms where all elements have comparable charge densities. Thus the scattering intensities of light and heavy elements are more balanced.<sup>[7]</sup> Here we present the direct imaging of the oxygen sub-lattice in beam sensitive, binary orthorhombic  $(\text{Mo}, \text{V})\text{O}_x$ . Images were recorded with a double corrected JEOL ARM 200F equipped with a cold field emission gun (CFEG) using HAADF and ABF detectors.

$(\text{Mo}, \text{V})\text{O}_x$  crystallizes in an orthorhombic structure (Pba2) closely related to the so-called M1 phase of  $\text{MoVTeNbO}_x$  (ICSD no. 55097, Figure 1).<sup>[8]</sup> It has been considered as catalyst in the oxidative activation of short-chain alkanes in the light of prospected raw material changes from crude oil to natural gas.<sup>[9]</sup> The obtained ABF-STEM images enable a direct measurement of the metal-oxygen bond angles for the different metal sites. Although the measured distortions correspond to a projection onto the basal plane, they give a hint on the oxidation state of each metal site.<sup>[10]</sup> Our findings are compared with Rietveld refined X-ray diffraction (XRD) data and electron paramagnetic resonance (EPR) spectroscopy.

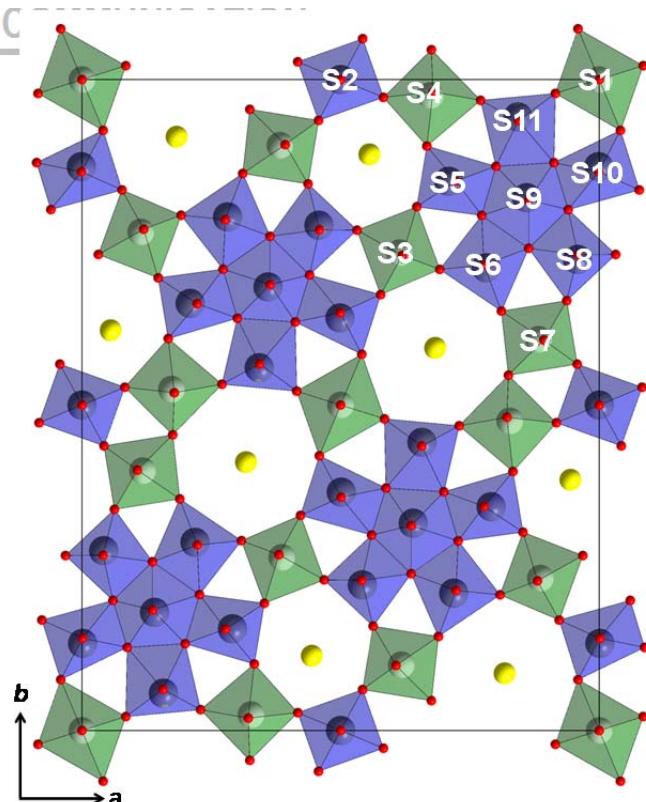
Aberration-corrected HAADF-STEM imaging has been used before<sup>[2, 11]</sup> to directly observe the characteristic metal framework of the orthorhombic  $(\text{Mo}, \text{V})\text{O}_x$  structure in the [001] projection. It provided valuable insights on different metal site occupancies and defect structures.<sup>[2, 12]</sup> In the case of highly crystalline  $(\text{Mo}, \text{V})\text{O}_x$  (Figure SI 1), the analysis of HAADF images (Figure 2A) showed a similar trend in the Mo site occupancy (Figure SI 2). Using the labelling scheme suggested by DeSanto<sup>[8]</sup> et al., the Mo content in the respective sites decreases in the order  $S9 \approx S5 \approx S6 > S8 \approx S10 \approx S11 > S2 > S4 \approx S3 \approx S7 > S1$ . This result is in good agreement with the preferential positions of Mo and V obtained by Rietveld refinement of the XRD data (Figure 1, Table 1 and Table SI 1). However, occupancies diverge slightly from observations reported previously, thus indicating a certain chemical flexibility of orthorhombic  $(\text{Mo}, \text{V})\text{O}_x$ . Variations in the Mo and V distribution could be related to the omitting of the thermal treatment after hydrothermal synthesis. may also arise from the fact that the present material is a product of hydrothermal synthesis that was not thermally treated. It is important to note here that STEM is a very local method and therefore allows resolving statistic occupation of inequivalent

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201xxxxx>.((Please delete if not appropriate))



sites for individual unit cells (Figure SI 3), whereas XRD averages over the whole sample.

**Figure 1.** Polyhedron model of the orthorhombic  $(\text{Mo},\text{V})\text{O}_x$  structure viewed along [001] obtained from Rietveld refined XRD pattern (Figure SI 4 and 5). Mo or V dominated, channel and oxygen sites are denoted by blue or green polyhedra/atoms, yellow and red atoms, respectively.

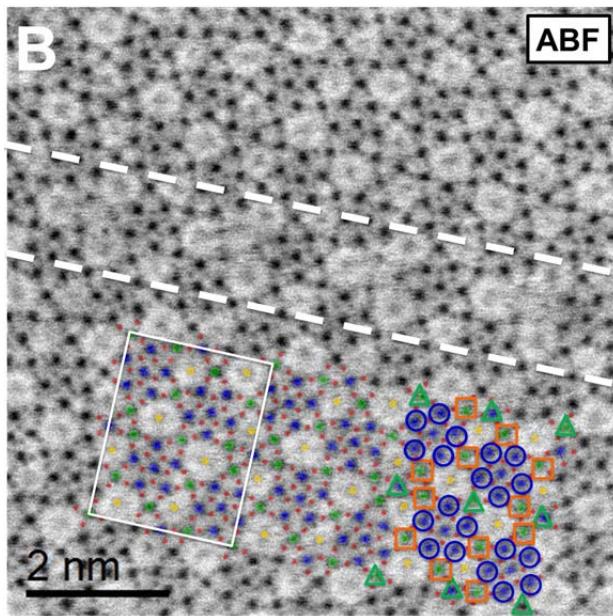
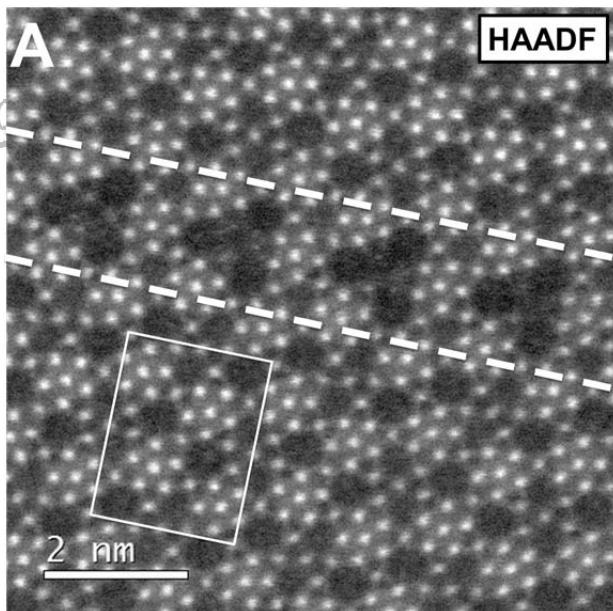
The simultaneously recorded annular bright field (ABF)-STEM image is depicted in Figure 2B. In ABF, channels appear bright, whereas individual metal and oxygen sites appear dark. As opposed to the HAADF, the oxygen columns in the vicinity of the metal sites can clearly be observed in the ABF images. In agreement with the XRD measurements (Figure 1, Figure SI 4 and 5), ABF reveals that heptagonal<sup>[14]</sup> and hexagonal channels exhibit additional electron density indicating at least a partial occupancy of both channels. Interestingly, the highly localized contrast due to the oxygen columns indicates a relative confined distribution of O atoms, suggesting an equal distortion of the  $\text{MO}_6$  octahedra stacks along [001] columns, regardless of the mixed Mo/V ratio. If the distortion at one site would vary, a diffuse contrast due to oxygen columns would be expected. The direct imaging of the metal oxygen polyhedra provides information about bond angles that can otherwise only be obtained by a combination of different physical methods. However, direct measurement of structural parameters requires distortion free imaging. To validate the absence of scan distortions a Pt reference sample was investigated using the same settings (see Figure SI 6). Improved room design and the high stability of modern TEM platforms allow distortion free imaging and abstraction of structural parameters as demonstrated by several recent publications.<sup>[15]</sup> The STEM images in Figure 2 and the measured angles correspond to a 2D

projection of  $(\text{Mo},\text{V})\text{O}_x$ . Thus, the apical M-O bonds are not accessible. The measured bond angles of the different metal sites in  $(\text{Mo},\text{V})\text{O}_x$  are listed in Table 1, Table SI 1 and are schematically illustrated in Figure 2B. Almost no distortion was obtained in the basal plane of the S1 and S2 sites, medium distortions were measured at the S3, S4 and S7 sites, and the highest distortions were observed for the metal sites S5, S6, S8, S9, S10, and S11, which are located in the pentagonal units.

The distortion in transition metal oxides is a result of symmetry breaking due to energy minimization and depends on the spin configuration of the central cation<sup>[10]</sup> and the local surrounding.<sup>[16]</sup> Fully oxidized polyhedra consisting of Mo or V are known to always show a high out-of-center distortion tendency towards various directions<sup>[8, 10]</sup> due to their ability to form stable "molybdenyl" or "vanadyl" ( $\text{M}=\text{O}$ ;  $\text{M}=\text{Mo},\text{V}$ ) species. Structurally, the M1 phase represents a group of non-stoichiometric oxides such as  $\text{Mo}_5\text{O}_{14}$ ,  $\text{Mo}_8\text{O}_{23}$  or  $\text{Mo}_{17}\text{O}_{47}$ .<sup>[17]</sup>  $\text{Mo}_8\text{O}_{23}$  for instance also exhibits a complex framework, composed of distorted edge shared octahedra hosting  $\text{Mo}=\text{O}$  species and less distorted bands of corner shared polyhedra.<sup>[18]</sup> In the case of vanadium,  $\text{V}^{5+}$  polyhedra are generally distorted through one shortened bond length forming the characteristic  $\text{V}=\text{O}$  bond.<sup>[10b, 19]</sup> While the strong distortion in highly oxidized Mo generally arises from a shortening of two metal oxygen bonds, in vanadium only one bond is compressed.<sup>[18-19]</sup> It has further been highlighted that the majority of  $\text{Mo}^{6+}$  cations tend to shift towards edges of the corresponding octahedra<sup>[10b]</sup>, leading to the occurrence of significant changes in the projected metal oxygen bond angles. In the case of fully oxidized V, the metal centres are known to be mostly shifted towards the vertices<sup>[10b]</sup>, thus resulting in lower projected bond distortions. This is reflected in our measured metal-oxygen bond angles which are highest for the molybdenum oxide octahedra (Table 1 and Table SI 1) in the pentagonal bipyramidal.

Based on the measured projected distortions we therefore propose that medium and highly distorted sites (S3, S4, S7, S5, S6, S8, S10, and S11) contain empty d- orbitals and accommodate highly charged V and Mo cations. In contrast, almost no distortions are observed for symmetric S1 and S2 sites. Thus, these sites might exhibit an increased probability for hosting one d- electron at the respective metal centers. Finally, in the case of the pentagonal bi-pyramidal S9 site, no strong distortions were observed, although XRD data and HAADF-STEM analysis reveal that it is mainly occupied by Mo (Figure 2B, Table 1) and, according to charge neutrality, it should be in a  $\text{d}^0$  oxidation state. In the case of the pentagonal bi-pyramidal we can therefore not draw conclusions about the relation between distortion and d-occupancy.

**Figure 2.** A) Atomic resolution HAADF-STEM image and simultaneously recorded ABF-image (B) of  $(\text{Mo},\text{V})\text{O}_x$ . The white rectangles in (A) and (B) display the orthorhombic unit cell. The white dashed lines in (A) and (B) denote a trigonal intergrowth. In (B) Mo, V dominating metal, channel and oxygen sites are highlighted in blue, green, yellow and red, respectively. The inset in (B) represents a simulated ABF image of  $(\text{Mo},\text{V})\text{O}_x$  with a thickness of



16 nm. For simulation the Rietveld refined structure was used. In addition, metal sites with high, intermediate and no distortions are indicated by blue circles, orange squares and green triangles, respectively. The original ABF image is given in the SI (Figure SI 7 and Figure SI 8).

To verify the presence of unpaired electrons an EPR measurement was conducted. The corresponding spectrum (Figure SI 9) can be fitted by two broad featureless signals and two signals containing hyperfine splitting (Figure SI 10). The g-factors for the broad signals are typical for strongly interacting V (or Mo) species with 3d (or 4d) electrons. These features are indicating the presence of two distinguishable metal sites in the bulk phase and were therefore used for correlation. The signals with resolved hyperfine structure correspond to isolated  $^{51}\text{V}^{4+}$  in an axial crystal field. Quantification of the spin numbers in the sample under the assumption that only  $d^0$  and  $d^1$  cations are present, reveals that at least 1-2% of the metals carry unpaired d-electrons (Table SI 2-5). In line with our assignment, the results could be translated to the presence of  $d^1$  electrons at the S1 and S2 site. It should be mentioned that the EPR detected amount of unpaired electrons represents a minimum value for  $d^1$  electrons present in the unit cell of  $(\text{Mo},\text{V})\text{O}_x$ .

**Table 1.** Measured oxygen-metal-oxygen bond angles within the basal plane of a low, medium and high distorted metal site, , preferred metal site occupation, and proposed oxidation states of Mo and V in the orthorhombic  $(\text{Mo},\text{V})\text{O}_x$  structure. Additional bond angles for various metal sites are listed in the SI (Table SI1).

oxygen site <sup>[a]</sup>	metal site	oxygen site <sup>[a]</sup>	bond angle <sup>[b]</sup> /°	metal <sup>[c]</sup>	population /at.% <sup>[d]</sup>	$d^1$ (OS) <sup>[e]</sup>
O26	S1	O13	90 <sup>[f]</sup>	V	87	high
O13	S1	O26'	90±1			(4+)
O26'	S1	O13'	90 <sup>[f]</sup>			
O13'	S1	O26	90±1			
O30	S3	O17	88±4	V	69	low
O17	S3	O14	97±3			(5+)
O14	S3	O15	89±4			
O15	S3	O30	85±3			
O19	S5	O30	109±2	Mo	90	low
O30	S5	O18	83±4			(6+)
O18	S5	O22	73±4			
O22	S5	O19	95±4			

[a] A oxygen site map is given in the SI (Figure SI 11). [b] Measured metal-oxygen bond angles in the basal plane. Given numbers are averages of different spots. [c] Preferred metal at the corresponding metal site as determined from the XRD data (Figure SI 5) and HAADF-STEM image (Figure 2A and Figure SI 2). [d] Occupancy of the dominating metal as obtained from XRD. The difference to 100% corresponds to the minor element. [e] Probability of realizing a  $d^1$  state and proposed oxidation state. [f] Symmetry centres: The angle of neighbouring metal-oxygen bonds has to be 180°.

Our assignments of the metal site occupancy, distortion in the oxygen sub-lattice and oxidation state based on STEM micrographs are in very good agreement with XRD and EPR measurements. The combination of edge and corner shared M-O polyhedra (M=Mo, V) with different degrees of distortion relieve lattice strain and lead to the realization of this energetically favoured, complex network structure. Such structures can be obtained by Mo or V since they are able to form discrete molybdenyl ( $\text{Mo}=\text{O}$ ) and vanadyl ( $\text{V}=\text{O}$ ) species, respectively. As the distortions are also affected by the electronic configuration, imaging of distortions in the oxygen sub-lattice enables a way to conclude on the oxidation state. The knowledge of the oxidation state of each single metal site will contribute to a better understanding of the redox chemistry of these materials and their function as prospective catalysts. Contrary to the HAADF-STEM image which gives the impression of empty channels which cannot be found by gas adsorption, the ABF image reveals occupied channels. This result further underlines the power of modern chemical TEMs equipped with an ABF detector to verify the filling of nominal channels in inorganic structures. This report demonstrates that we are getting closer to Feynman's wish of understanding the atomic

arrangement by just looking at it. In conclusion, we have demonstrated that modern electron microscopy provides detailed chemical information that could otherwise only be obtained by a combination of different analytical methods and could therefore be labelled as chemical electron microscopy (ChemEM). Abstracting local oxidation states from the atomic position in images provides an alternative to electron energy loss spectrometry for cases of beam sensitive materials.

## Experimental Section

The (Mo,V) oxide (FHI-SN: 11345) was prepared by hydrothermal synthesis and analysed without further thermal treatment.<sup>[14]</sup> Details regarding synthesis and the applied analytical techniques are summarized in the Supporting Information.

## Acknowledgements ((optional))

JN thanks BasCat for a fellowship. The authors acknowledge Norbert Pfänder for colorizing the ABF-STEM image.

**Keywords:** transmission electron microscopy • annular bright field • bond angles • light elements • Chemical electron microscopy

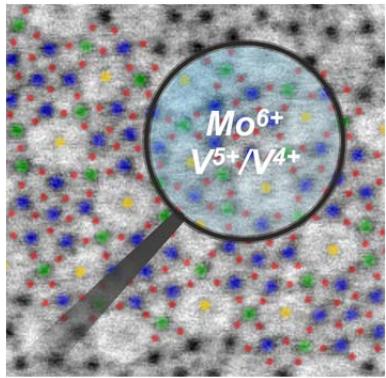
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**Entry for the Table of Contents (Please choose one layout)**

Layout 1:

**COMMUNICATION**

A beam sensitive (Mo,V) mixed oxide has been studied by ABF-STEM. The recorded micrographs show the oxygen sub lattice and directly reveal the local distortion in the metal oxygen octahedra. From the observed distortion, conclusions on the oxidation state of each metal site can be drawn just by looking at the atomic arrangement.

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Layout 2:

**COMMUNICATION**

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