



# Electronic structure studies of $\gamma$ - $V_2O_5$ : Ab-initio calculations and EELS measurements



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## Introduction

Vanadium oxides merit special attention because of their outstanding structural flexibility combined with chemical and physical properties which are of interest for catalytic and electrochemical applications. Specially  $V_2O_5$  is an essential ingredient to heterogeneous catalysis and its electronic and structural properties have been widely studied.

This work presents band structure calculations of  $\gamma$ - $V_2O_5$  [1], a polymorph of the more common known  $\alpha$ - $V_2O_5$ .

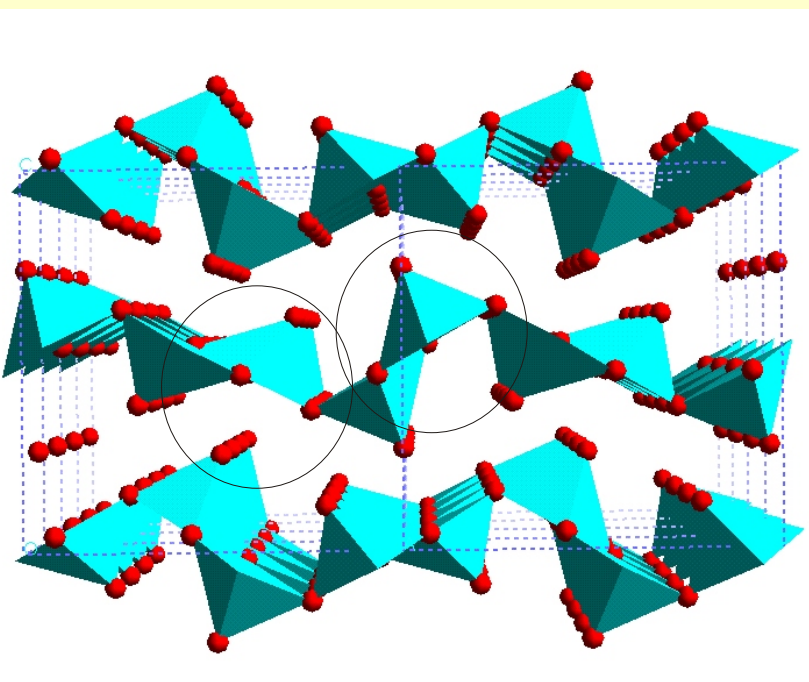
The basic structural  $VO_5$  units of  $\gamma$ - $V_2O_5$  and  $\alpha$ - $V_2O_5$  are compared and related to differences in their electronic structure. A detailed understanding of the relation between geometric and electronic structure is essential since this basic structural unit is also common to the industrial used VPO catalysts.

## Calculation and Experiment

Band structure calculations of the density of states (DOS) were performed using the full potential linear augmented plane wave code WIEN2k [2]. In the calculations the generalized gradient approximation (GGA) was used as exchange-correlation potential and the core hole left by the excited electron was neglected.

In order to compare the theoretical results with experiments, the O-K ELNES (Energy Loss Near Edge Structure) was simulated and compared to EELS spectra recorded from  $\gamma$ - $V_2O_5$  nanorods [3] and  $\alpha$ - $V_2O_5$ . EELS was performed using a Philips CM 200 field emission transmission electron microscope equipped with a Gatan energy filter. The microscope was operated at 200kV with an energy resolution, estimated from the full-width at half maximum of the zero-loss peak, of 1 eV.

$\gamma$ - $V_2O_5$   
Orthorhombic (62\_Pnma)  
**a = 9.946(0) Å,**  
**b = 3.585(0) Å,**  
**c = 10.042(0) Å.**



$\alpha$ - $V_2O_5$   
Orthorhombic (59\_Pmmn)  
**a = 11.512 Å,**  
**b = 3.564(0) Å,**  
**c = 4.368(0) Å.**

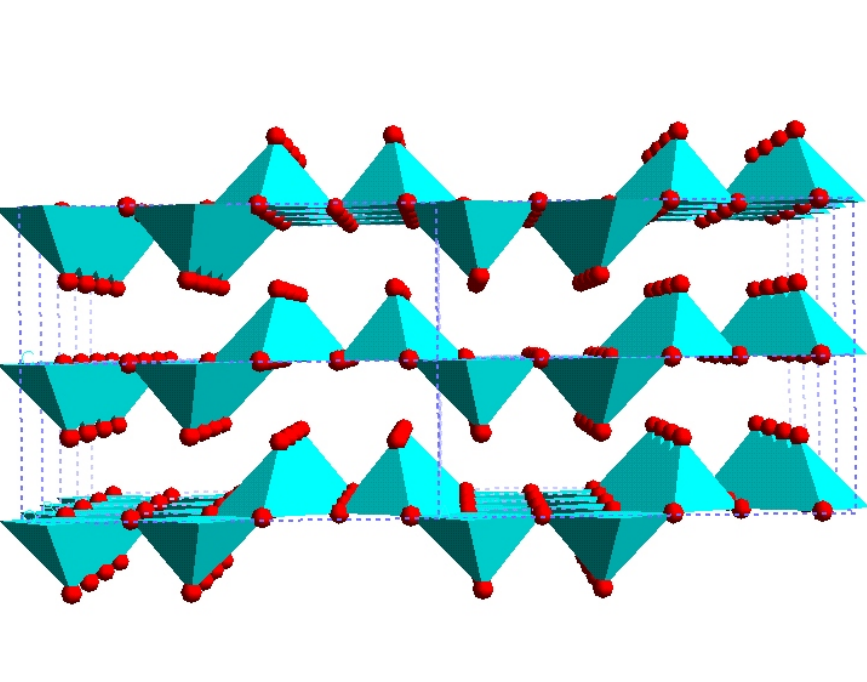


Fig 1 Representation of the two polymorphous  $V_2O_5$  structures  $\gamma$ - $V_2O_5$  (left) and  $\alpha$ - $V_2O_5$  (right)

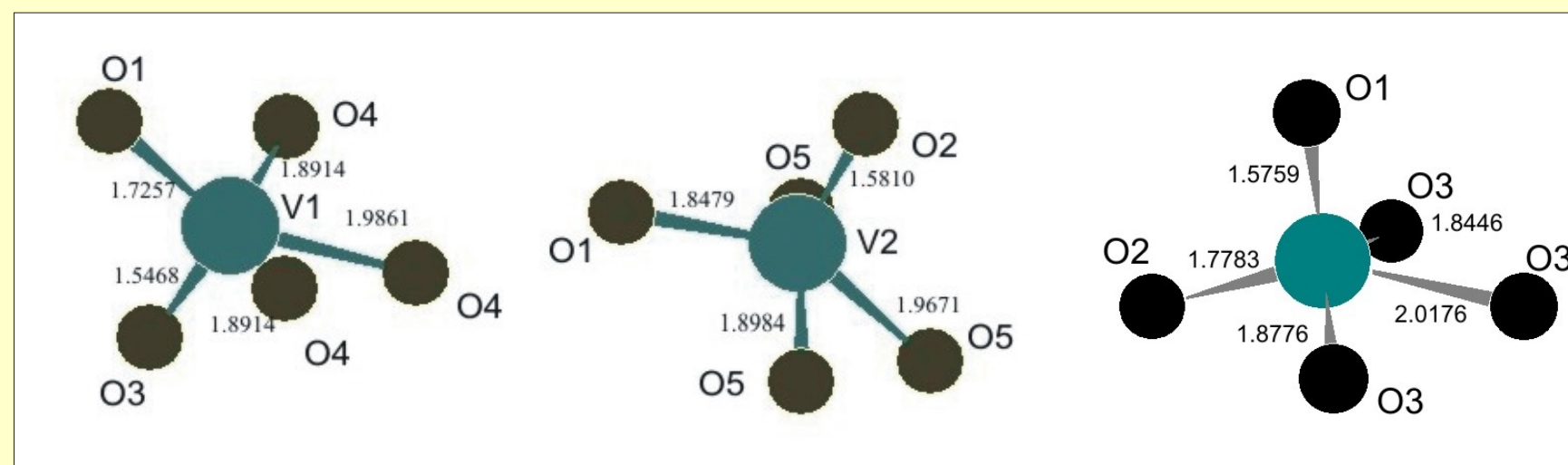


Fig 2 The three different  $VO_5$  pyramids for which the atom projected density of states are compared and structural effects are discussed. V1 and V2 indicate the two structurally different  $VO_5$  pyramids of  $\gamma$ - $V_2O_5$ .

## Structure

The structure is set up by layers of edge and corner sharing  $VO_5$  pyramids sticking out at both sides of the layer. As opposed to  $\alpha$ - $V_2O_5$ , where all V=O vanadyl bonds are oriented along c, the double chains of edge sharing pyramids are tilted relatively to each other in  $\gamma$ - $V_2O_5$  (Fig. 1). As a consequence, there exist two structurally different  $VO_5$  pyramids. The first one at the V1 site can also be thought of as a bi-pyramidal ( $VO_6$ ) by including the weak interlayer bond to the vanadyl oxygen of the adjacent layer. The second  $VO_5$  pyramid at the V2 site is positioned in such a way that no oxygen atom lies in close vicinity of the basal plane. Each of the two pyramids contains three structurally different oxygens, but in total, due to the linking via one common oxygen, there exist five different oxygens and two different vanadiums in  $\gamma$ - $V_2O_5$ . The primitive cell comprises four formula units. It is worthwhile to mention here that  $\gamma$ - $V_2O_5$  undergoes a transformation into the normal form of  $\alpha$ - $V_2O_5$  near 340 °C [1].

| Bond length         | Vanadyl-Oxygen   | Bridge-Oxygen    | Chain-Oxygen               |
|---------------------|------------------|------------------|----------------------------|
| $\gamma$ - $V_2O_5$ | 1.5468 Å (V1-O3) | 1.7257 Å (V1-O1) | 1.8914 Å, 1.9861 Å (V1-O5) |
| $\gamma$ - $V_2O_5$ | 1.5810 Å (V2-O2) | 1.8479 Å (V2-O1) | 1.8984 Å, 1.9671 Å (V2-O4) |
| $V_2O_5$ (bulk)     | 1.5759 Å (V-O1)  | 1.7783 Å (V-O2)  | 1.8776 Å, 2.0176 Å (V-O3)  |

## Theory/DOS

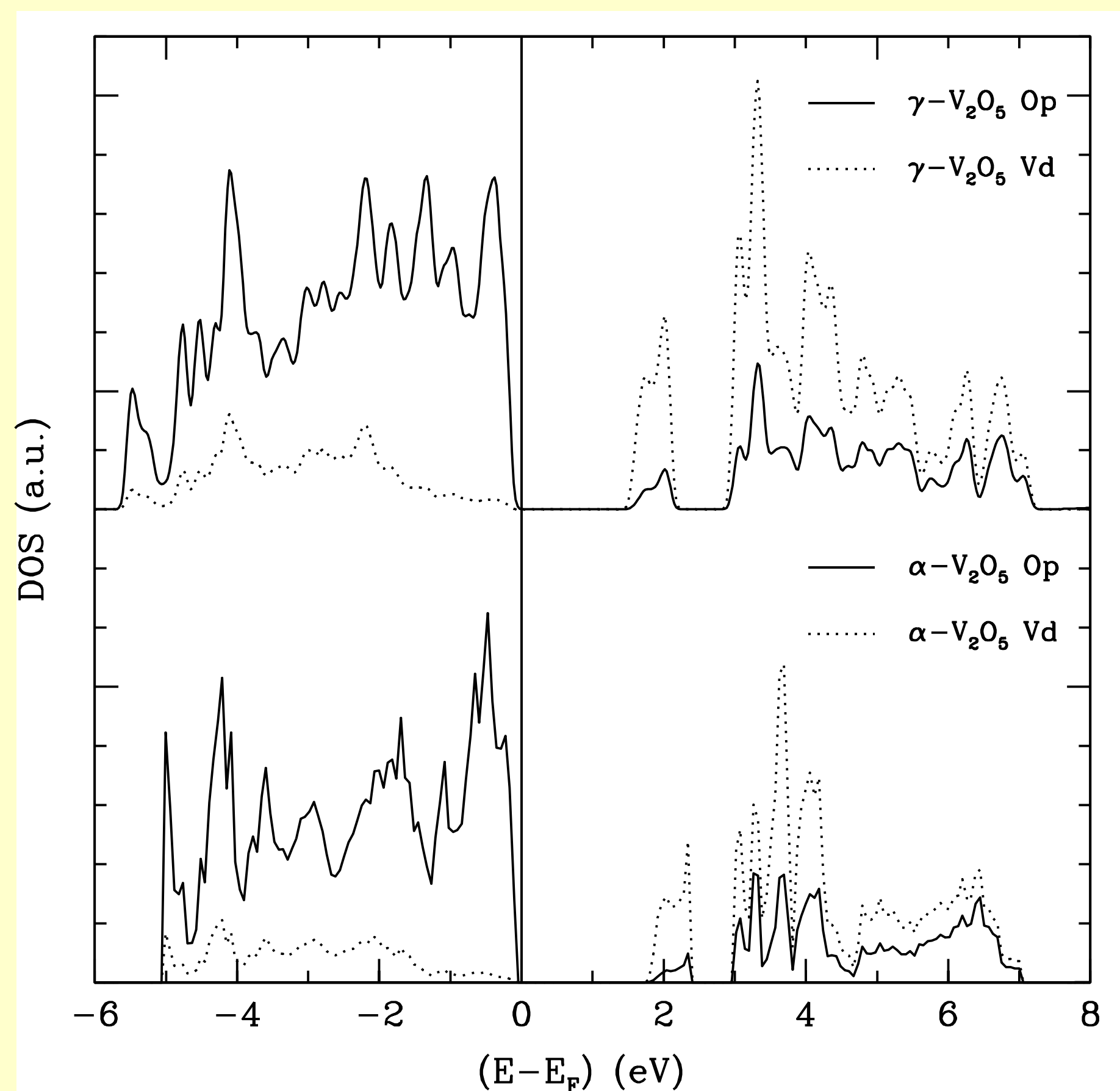


Fig. 3 presents the calculated DOS of the oxygen 2p and vanadium 3d states which mainly define the chemical and physical properties and attest the close relation between the structure of the two compounds.

The valence bands mainly consist of oxygen 2p states, whereas the conduction bands mainly comprise the unoccupied vanadium 3d states. Common features in the oxygen and vanadium DOS reflect a substantial degree of hybridization between oxygen 2p and vanadium 3d states of the two  $V_2O_5$  structures.

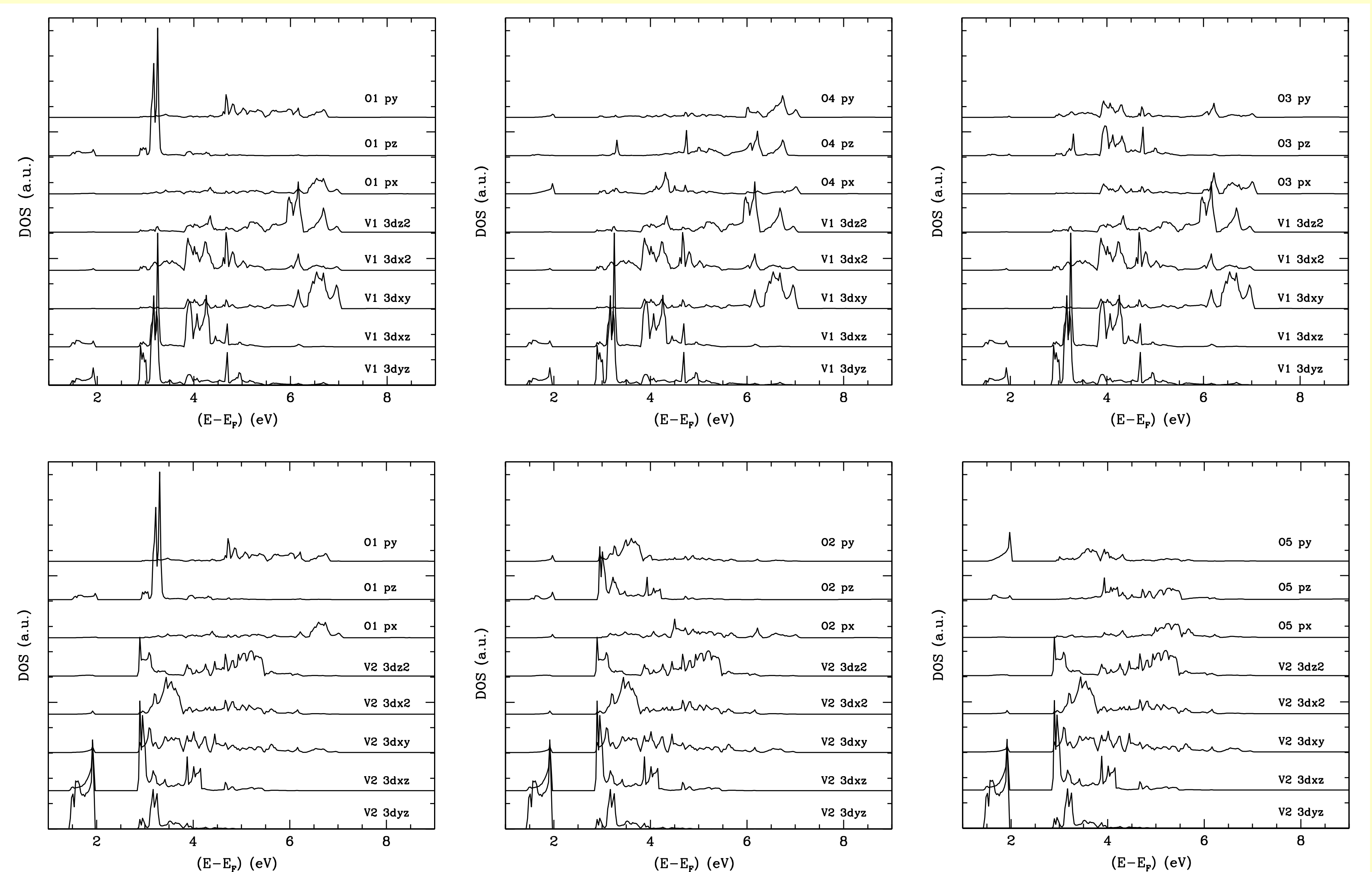


Fig. 4. The site and angular momentum projected DOS at the differently distorted  $VO_5$  pyramids. The stronger distortion at the V1 center is reflected by a higher dispersion of the d states and a clear splitting into  $t_{2g}$  and  $e_g$  forming states is visible. At the V2 center the crystal field splitting separates the  $3d_{z^2}$  from the other d states.

## Comparison to experiment/EELS

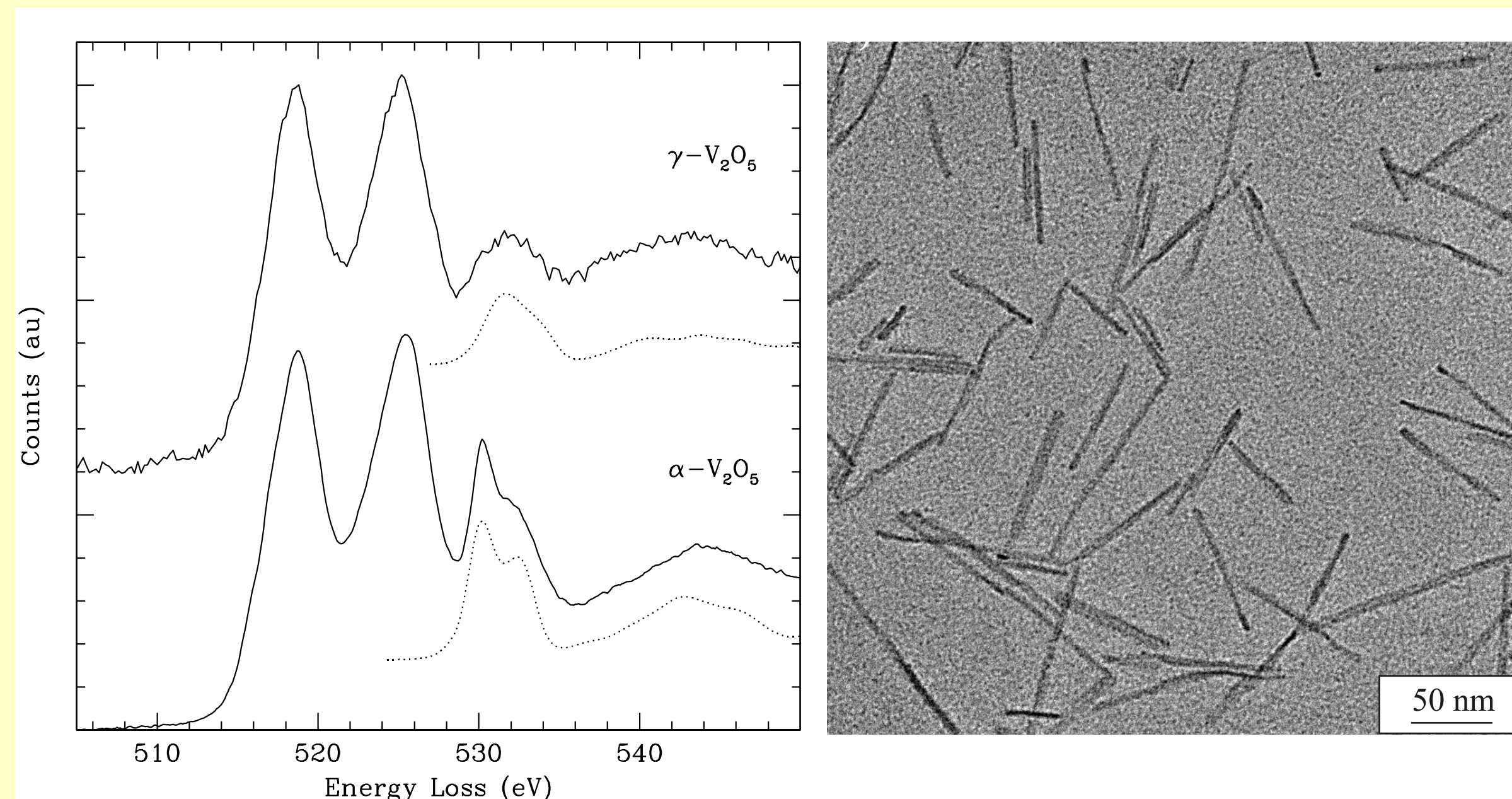


Fig 5. a) Simulated (dotted line) and experimental EELS spectrum. The first two features are attributed to the excitations from  $V 2p_{3/2}$  and  $V 2p_{1/2}$  core levels to the unoccupied  $V 3d$  states, respectively. The oxygen K edge around 530 eV is due to the excitation of O1s electrons to final 2p states in  $\gamma$ - $V_2O_5$  or hybridization with a vanadium 3d state. The different shape of the O K-edge fine structure directly reflects the different geometric and electronic structure of the two polymorphs. b) TEM pattern of nanorods synthesized in reverse micelles.

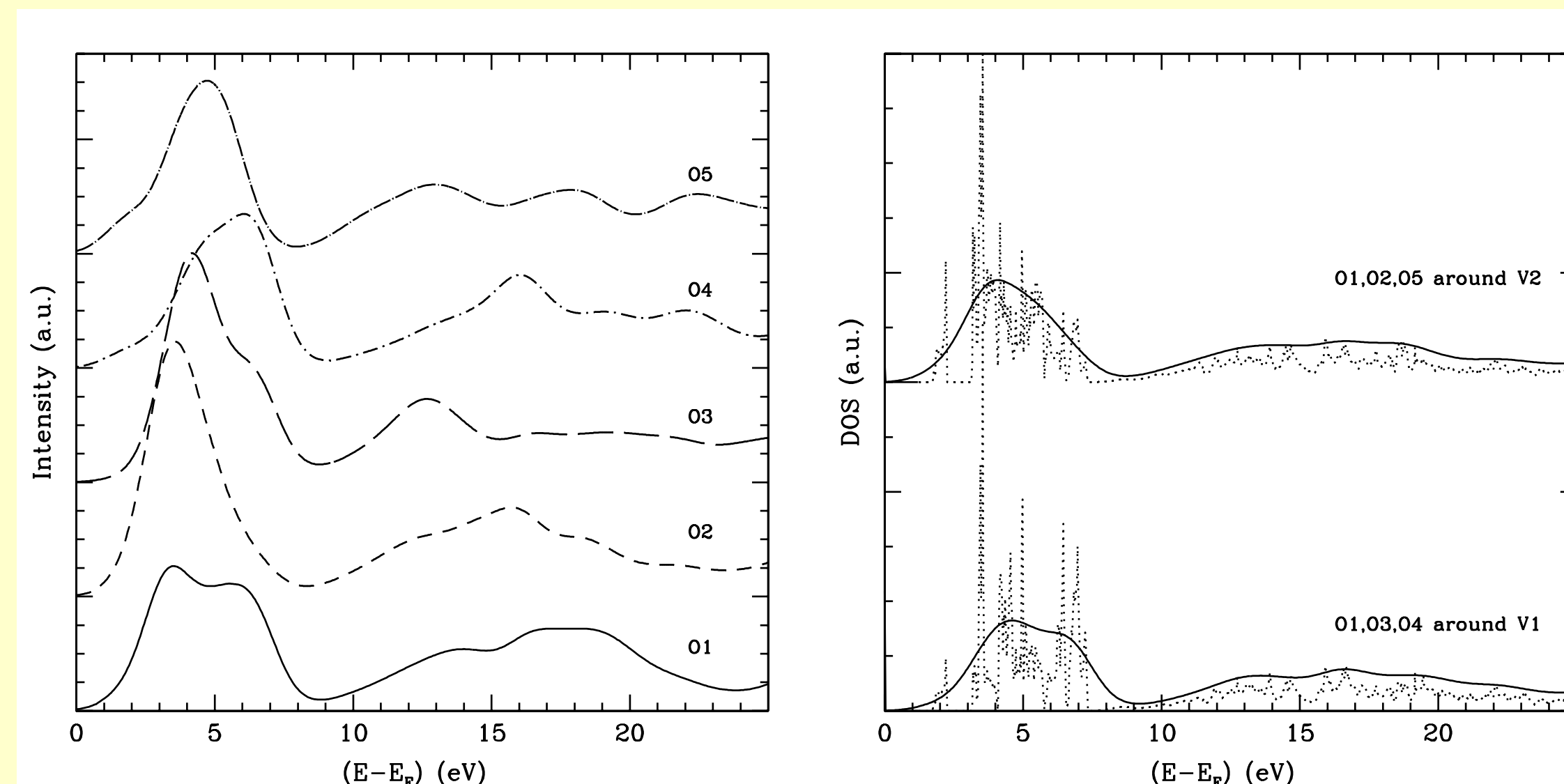


Fig. 6 Five differently coordinated oxygen atoms contribute to the spectrum and the total O K spectral weight is the sum of these contributions, of which each has its individual shape. Also shown are the DOS and the sum of oxygen contributions at the two different  $VO_5$  pyramids (V1 and V2 site) of  $\gamma$ - $V_2O_5$ .

## Summary

Bandstructure calculations of a new polymorph of  $V_2O_5$  were performed in order to correlate the electronic structure to the local geometric structure of differently coordinated vanadium atoms in  $\gamma$ - $V_2O_5$ . The nice fit between the calculated EELS spectra and experimental results proves the capability of assigning features in the spectra to related transitions and to gain insight into the local electronic structure.

## Bibliography

- [1] J. M. Cocciantelli, P. Gravereau, J. P. Doumerc, M. Pouchard, P. Hagenmuller, *J. of Sol. State Chem.* 1991, **93**, 497.
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