Influence of the vacuum interface on the charge distribution in V2O3 thin films

Udo Schwingenschlögl, Raymond Frésard, Volker Eyert

Influence of the vacuum interface on the charge distribution in V$_2$O$_3$ thin films

View the article online for updates and enhancements.

Related content

- Surface effects on oxide heterostructures
  U. Schwingenschlögl and C. Schuster

- Embedded Peierls instability
  V Eyert, R Horny, K-H Höck et al.

- LDA+DMFT implemented with the pseudopotential plane-wave approach
  G Trimarchi, I Leonov, N Binggeli et al.

Recent citations

- The importance of the on-site electron–electron interaction for the magnetic coupling in the zigzag spin-chain compound In$_2$VO$_5$
  H Wang and U Schwingenschlögl

New Journal of Physics

Influence of the vacuum interface on the charge distribution in V_2O_3 thin films

U Schwingenschlögl[1]**, R Frésard**[2] **and V Eyert**[3,4]

[1] KAUST, PCSE Division, PO Box 55455, Jeddah 21534, Saudi Arabia
[2] Laboratoire CRISMAT, UMR CNRS-ENSICAEN(ISMRA) 6508, and IRMA, FR3095, Caen, France
[3] Center for Electronic Correlations and Magnetism, Institute for Physics, University of Augsburg, 86135 Augsburg, Germany
E-mail: eyert@physik.uni-augsburg.de

Abstract. The electronic structure of V_2O_3 thin films is studied by means of the augmented spherical wave method as based on density functional theory and the local density approximation. We establish that the effects of charge redistribution, induced by the vacuum interface, in such films are restricted to a very narrow surface layer of ≈ 15 Å thickness. As a consequence, charge redistribution can be ruled out as a source of the extraordinary thickness dependence of the metal–insulator transition observed in V_2O_3 thin films of ~ 100–1000 Å thickness.

Contents

[4] Author to whom any correspondence should be addressed.

IOP Institute of Physics ◆ DEUTSCHE PHYSIKALISCHE GESELLSCHAFT

1. Introduction

Over the last few decades, V_2O_3 has been investigated extensively by both experiment and theory—and is still a topic of great interest (see e.g. [1, 2] and the literature given therein). Today, V_2O_3 thin films are receiving increased attention, particularly because the thin film geometry appears to strongly modify the electronic properties of the material, as is most clearly demonstrated by the famous metal–insulator transition observed in bulk V_2O_3 as a function of temperature, pressure or doping [3]. It is known that even a small alteration of the crystal structure, by Cr substitution [4] or application of external pressure [5], can have a serious effect on the metal–insulator transition in bulk material. Therefore, it would not be at all surprising if structural modifications induced by the thin film geometry had similar severe implications.

Recently, the observation of a thickness-dependent metal–insulator transition in ultrathin V_2O_3 films was attributed to the increasing c/a lattice parameter ratio (decreasing a, increasing c) because of interaction with the substrate [6]. However, this conjecture has been refuted by both x-ray diffraction studies for high quality films [7, 8] and density functional calculations [9]. In fact, the experiments point to a very complex thickness dependence of the lattice parameters with unsystematic changes of the c lattice constant for film thicknesses of ~ 100–1000 Å, thereby calling for a more in-depth study of electronic properties of these films. Indeed, in other systems, like the $LaAlO_3/SrTiO_3$ heterostructure [10], it has been shown that interfaces can seriously modify the electron density profile. A strong dependence of electronic properties on layer thickness has also been reported for hexagonal layer compounds such as WS_2 [11]. In the present case a systematic investigation is still missing.

In this paper, we aim at clarifying the influence of the vacuum interface on the electronic states of V_2O_3 thin films. At this interface, two possible scenarios may cause a significant reorganization of the electronic states: (1) local modification of the crystal structure and (2) charge redistribution due to broken symmetry at the vacuum interface. In general, charge redistribution due to a surface, similar to heterointerfaces, may induce a considerable deviation from the bulk properties, see e.g. [12]–[15]. Even though possibility (2) therefore seems to be promising, it is the aim of this paper to point out the limitations of such a mechanism for film thicknesses exceeding some 15 Å.

2. Computational method and technical details

Calculations are based on density-functional theory and the local density approximation (LDA). They were performed using the scalar-relativistic implementation of the standard augmented spherical wave (ASW) method (see [16], chapter 2 of [17] and references therein). In the ASW method, the wave function is expanded in atom-centered ASWs, which are Hankel functions and numerical solutions of Schrödinger's equation, respectively, outside and inside the so-called augmentation spheres. In order to optimize the basis set, additional ASWs were placed at carefully selected interstitial sites. The choice of these sites as well as the augmentation radii were automatically determined using the sphere-geometry optimization algorithm [18]. Self-consistency was achieved by a highly efficient algorithm for convergence acceleration [19]. The Brillouin zone integrations were performed using the linear tetrahedron method with an increasing number of **k**-points in order to check the convergence with respect to the granularity of the **k**-point grid [17, 20].
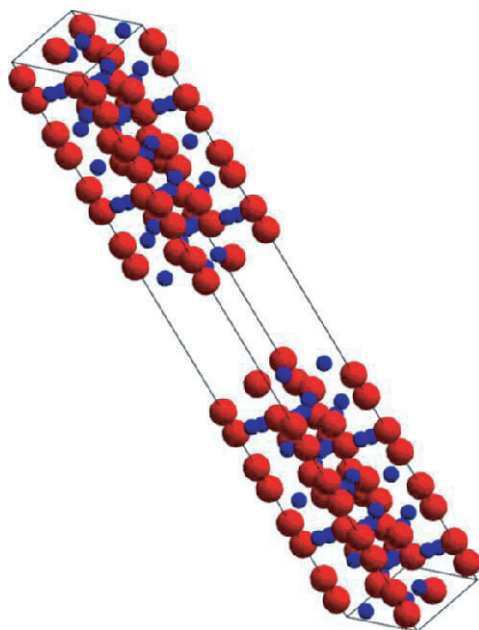
Figure 1. Slab used for modeling the V_2O_3 surface. Large and small spheres represent the V and O atoms, respectively.

The V_2O_3 surface was simulated by means of a fivefold superstructure of the canonical hexagonal unit cell. The latter comprises six formula units, i.e. six V layers along the (hexagonal) c-axis. These layers are separated by O layers, giving rise to VO_6 octahedra. For further details, see e.g. [21, 22] and the references therein. The lattice constants and fractional coordinates of the atoms were taken from [23]. The surface was then generated by removing all atoms from one of the five hexagonal unit cells, see figure 1, such that one of the resulting surfaces terminates with an O layer. This vacuum interface is the subject of the subsequent discussion.

In order to separate the charge redistribution due to broken crystal symmetry and changes in chemical bonding at the vacuum interface from the structural relaxation effects at the V_2O_3 surface, we will not include the latter in our considerations. In fact, structural relaxation is restricted to a very narrow range of about five atomic layers as has been pointed out in a detailed study by Kresse *et al* [24], which also provides an elaborate overview of the relevant literature. In contrast, we shall focus on the question of whether the charge redistribution coming with the removal of bonding partners could affect the behavior of a much thicker slab of several 100–1000 Å. Consequently, accounting for the near-surface structural modification is, on the one hand, dispensable and, on the other hand, disadvantageous for a systematic analysis of the decay of charge redistribution effects.

Of course, in view of the strong electronic correlations present in V_2O_3, calculations beyond the standard LDA seem necessary. Indeed, while LDA fails to capture the metal–insulator transition of the bulk material, the latter could be successfully described using LDA + DMFT (Dynamical Mean Field Theory) [25, 26]. However, for the large supercell used in the present simulation of the surface, the rather complex LDA + DMFT calculations would be beyond present-day computational facilities. Even more important, previous LDA + DMFT studies revealed that the strong electronic correlations come into play via the narrowing of bands
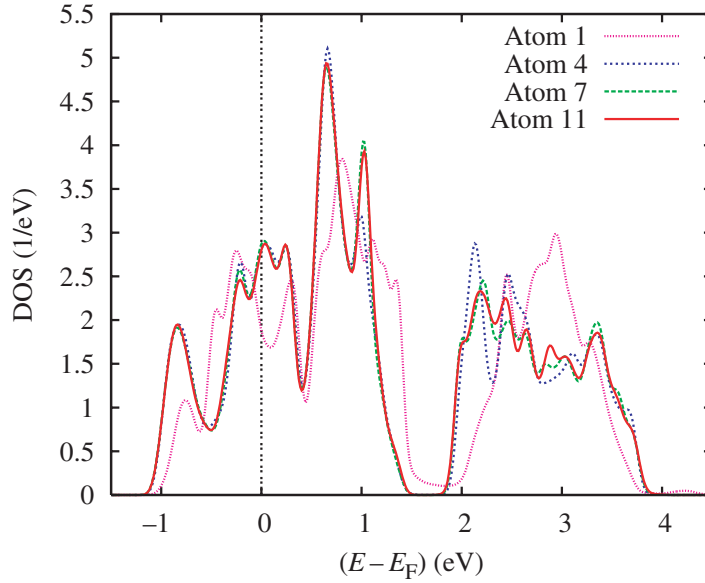
Figure 2. Site-projected partial V 3d DOS for a series of V sites in a V_2O_3 thin film. Numbering of the V atoms corresponds to their distance from the surface.

as calculated within the LDA, which occurs on going from the crystal structure of the metal to that of the insulator. Hence, there is a clear signature already in the LDA bands indicating the metal–insulator transition. As a consequence, although LDA has turned out to be insufficient in describing the metal–insulator transition itself, it clearly signals its occurrence. For that reason, it is well justified to omit a full LDA + DMFT treatment as long as the LDA results are carefully interpreted.

3. Results

Due to the octahedral O-coordination of the V atoms in V_2O_3, the V 3d electronic bands (located around the Fermi level) are subject to a splitting in two subgroups. While the partially occupied t_{2g} manifold is found in the energy range from -1.2 to 1.4 eV, the unoccupied e_g^σ states extend from 1.7 to 3.7 eV. These two groups are clearly observed in figure 2, which depicts the site-projected V 3d density of states (DOS) as obtained for various atoms in the thin film. Atoms are numbered according to their distance from the surface, with atom 1 being located directly at the surface. We find that the shapes of the curves in figure 2 are closely related to each other. Only for atom 1, which is subject to the strongest interface effects, deviations are visible since half of the bonding partners are missing and the V–O bonding is therefore reduced. In fact, the DOS curves of atoms 7 and 11, which are separated from the surface by about 18 and 28 Å, respectively, virtually resemble the bulk DOS shape. For this reason, the decay of the interface-induced relaxation of the electronic states is found to be very fast.

In order to establish further insight into the above-mentioned decay, we display in figure 3 V 3d and O 2p partial DOSs in a wider energy range in the left column as well as orbital resolved V 3d partial DOSs in the right column. The nearly perfect splitting of the t_{2g} manifold into a_{1g} and e_g^π sub-groups traces back to the trigonal symmetry of the corundum lattice [25]. The partial
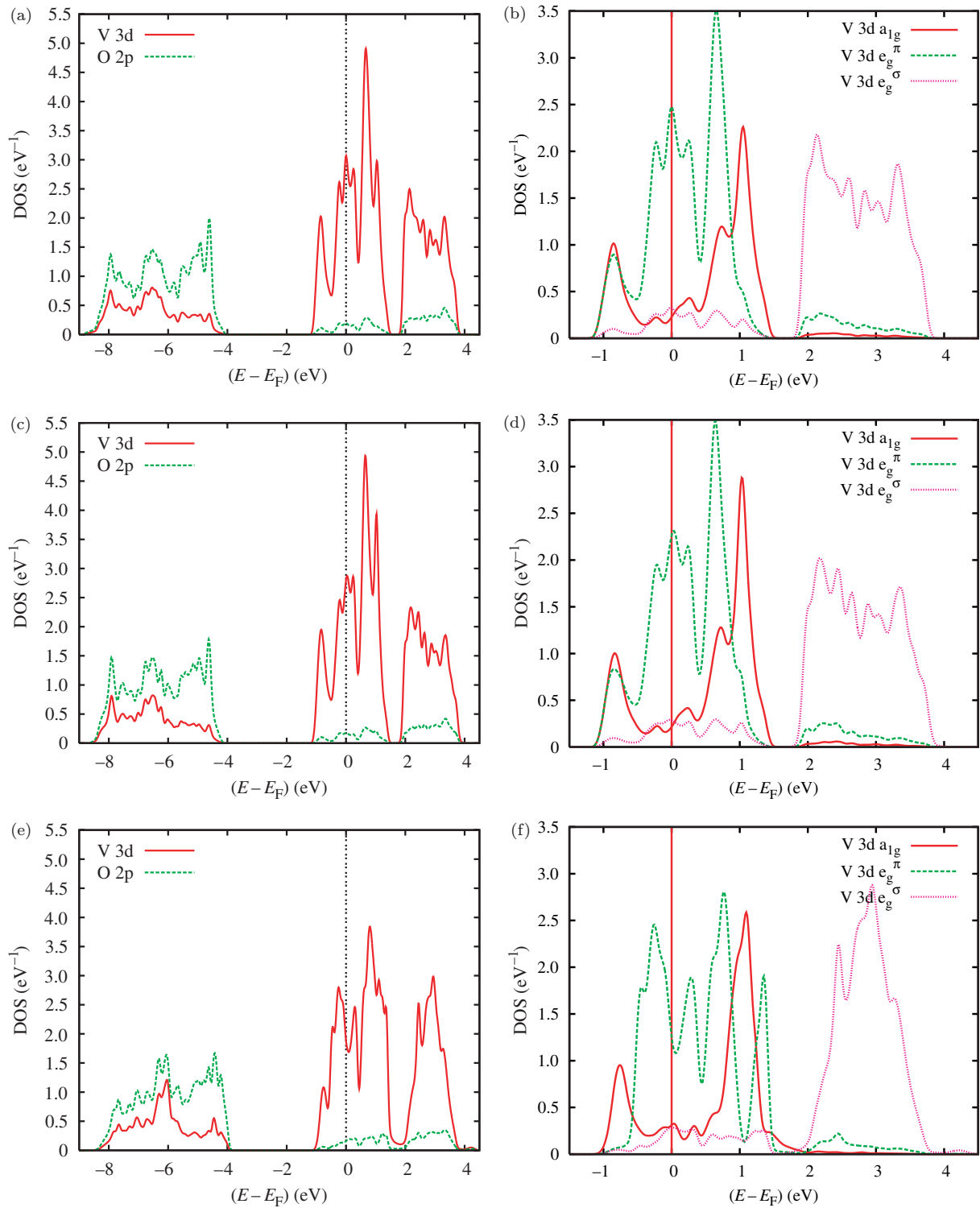
Figure 3. Partial V 3d and O 2p DOS (left) as well as V 3d symmetry components (right) for a VO_6 octahedron in bulk V_2O_3 (top row), separated by ≈ 28 Å from the surface of a V_2O_3 thin film (center row), and at the surface of a V_2O_3 thin film (bottom row). All DOS curves are per formula unit.
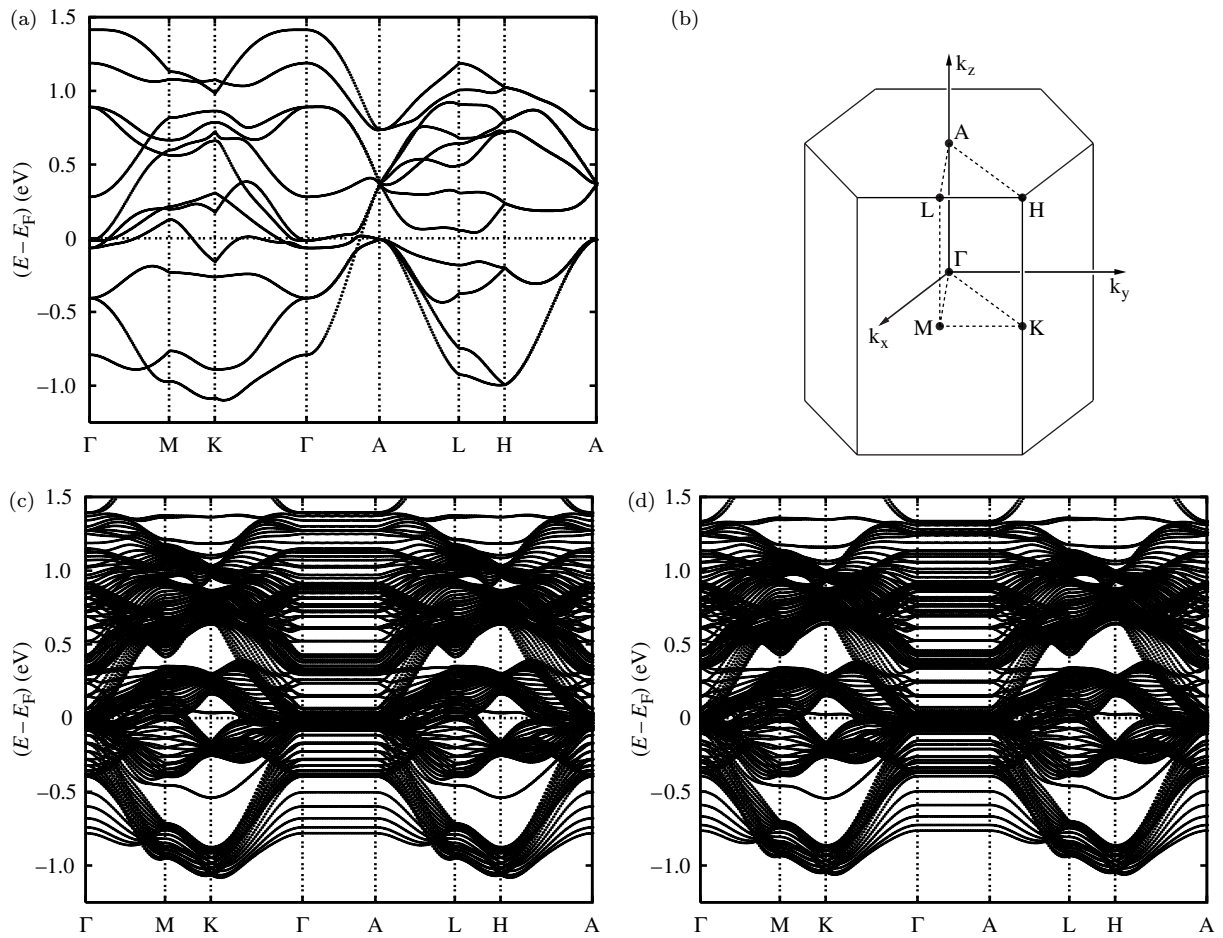
Figure 4. Electronic band structure of bulk V_2O_3 (top left), for high symmetry lines in the first Brillouin zone of the hexagonal lattice (top right), compared to a V_2O_3 thin film with bulk lattice constants (bottom left) and with a 1% elongated c lattice constant (bottom right).

DOS of V_2O_3 bulk (top row of figure 3) is almost identical to that found for a VO_6 octahedron in the thin film some 28 Å beneath the surface (center row of figure 3). This holds for both the O 2p and the V 3d states. In contrast, the surface VO_6 octahedron clearly shows distinct electronic relaxation effects of the local electronic states (bottom row of figure 3), which can be attributed to the modified chemical d–p bonding at the surface. In particular, for those V and O atoms, which miss a bonding partner due to the surface, we observe a reduction of the 3d and 2p occupation, respectively, of approximately 0.08 electrons. We point out again that in obtaining these results we did not take into account the V_2O_3 surface relaxation in order to distinguish between the electronic changes and the short-range structural distortions. Our results entail that the effect of the vacuum interface on the local electronic states, as reflected by the site-projected DOS, vanishes at about 15 Å below the surface. Charge redistribution induced by the surface is therefore restricted to the same narrow surface layer in which the structural relaxation is observed [24].

In a next step we turn to the discussion of **k**-resolved quantities and display the electronic bands in figure 4. The top row of figure 4 depicts the band structure of bulk V_2O_3 as well as the

non-primitive hexagonal Brillouin zone of the corundum lattice of V_2O_3, which here and in the following is used for representing findings of band structure calculations. The bulk results serve as a reference for comparison with the surface results given in the bottom left panel of figure 4.

Of course, the surface band structure comprises a lot more bands due to the simulation of the surface by the fivefold supercell of the surface slab as mentioned above. In this supercell, the increased number of different bands reflects the larger number of inequivalent atomic sites. V (and O) atoms with different distances to the vacuum are no longer equivalent from the crystallographic point of view. Furthermore, the dispersion along the high symmetry line Γ–A is strongly suppressed because this line corresponds to the direction perpendicular to the surface. Note that the construction of the surface slab in a fivefold supercell of the hexagonal V_2O_3 cell implies that the length of the line Γ–A is reduced to a fifth and that the electronic bands are folded back. In order to enable a straightforward comparison with the bulk data, the line Γ–A is artificially stretched to the original length in the slab band structure. With this in mind, we eventually find that the surface slab reproduces the characteristics of bulk V_2O_3 bands. In particular, there is no sign of an additional state, not present in the bulk, which could be responsible for the anomalous behavior of thin films.

It has been found, for V_2O_3 thin films, that the constants a and c of the corundum lattice deviate slightly, i.e. less than 1%, from their bulk values [7, 8]. In addition, we have shown that the influence of the a parameter change on the electronic structure is negligible [9]. Here, we investigate whether modifications of the c parameter may play a more important role by performing a surface slab calculation with the constant c increased by 1% as compared to the bulk. The results are depicted in the bottom right panel of figure 4, which uses the same representation as before. Comparison with the bottom left panel of figure 4 shows that an elongation of the c-axis does not lead to a qualitative change of the electronic states. The two band structures are, in fact, almost identical. Hence, the experimentally observed alterations of the V_2O_3 lattice parameters in a thin film influence the electronic states only marginally, as long as they are not accompanied by a relaxation of the atomic positions. Indeed, a substantial lattice relaxation has been advocated to interpret transport measurements [29].

To ensure that the thin film electronic structure fully resembles the bulk, a final step is necessary. We still have to exclude differences in the contribution of atomic orbitals to the different electronic states, since they would point at a modified chemical bonding. Orbitally weighted band structures are useful tools to address this question. Figure 5 gives an example of a prototypical V atom, some 28 Å below the surface. Very similar results are obtained for the neighboring V sites. In figure 5, the bars added to each state have a length proportional to the contribution of the 3d t_{2g} orbitals of the atom under consideration. States with minor 3d t_{2g} admixture are not depicted for clarity. For this reason, some of the bands shown in the bottom left panel of figure 4 are missing in figure 5. We observe that the selected V site contributes to the 3d t_{2g} bands in the entire energy range from −1.2 to 1.4 eV and thus perfectly reflects the behavior of a bulk atom, which is true for any atom located at least ∼15 Å below the surface. Charge redistribution as induced by the vacuum interface therefore has to be excluded as a possible source for the novel electronic properties of V_2O_3 thin films. We finally mention that in the case of a heterosystems like $LaAlO_3/SrTiO_3$ [27, 28], different charge redistributions have been obtained in LDA and LDA + U calculations. However, for the present system we do not find such a dependence.

In conclusion, our findings entail that neither the observed changes of the a and c lattice parameters in V_2O_3 thin films nor the response of the electronic system to the presence of
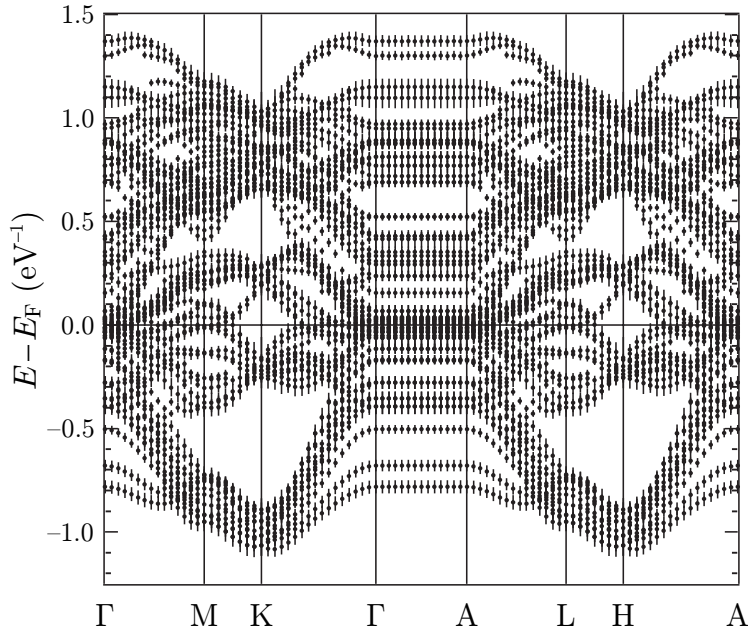
IOP Institute of Physics **Φ** DEUTSCHE PHYSIKALISCHE GESELLSCHAFT

Figure 5. Weighted electronic bands for a prototypical V atom in a V_2O_3 thin film, located $\approx 28\,Å$ beneath the surface. The length of the bars shown for each state is proportional to the contributions of this atom. States with a contribution below a certain threshold are omitted for clarity.

the vacuum interface can explain significant deviations from the electronic properties of bulk V_2O_3. Only next to the surface, i.e. in a narrow layer of at most $15\,Å$ thickness, is a charge redistribution observed. The same behavior has been found in calculations for other transition metal surfaces [30, 31].

Below the $15\,Å$ surface layer the electronic states are hardly modified by the vacuum interface. LDA + DMFT calculations have shown that the narrowing of the V 3d t_{2g} group of bands seen in the plain LDA DOS (which traces back to structural alterations [32]) is the essential criterion for obtaining a metal–insulator transition in bulk V_2O_3 [25, 26]. Because such a narrowing is not observed in our results, they contradict a transition for V_2O_3 thin films of $100–1000\,Å$ thickness, as long as a restriction of the structure relaxation to the surface layer is assumed. Conversely, only further changes of the atomic structure, probably in the entire thin film, can explain the experimental situation. A detailed study of the crystal structure over the entire thin film is thus required to settle this issue.

References

[1] Rodolakis F *et al* 2009 *Phys. Rev. Lett.* **102** 066805
[2] Borghi G, Fabrizio M and Tosatti E 2009 *Phys. Rev. Lett.* **102** 066806

IOP Institute of Physics ⬥ DEUTSCHE PHYSIKALISCHE GESELLSCHAFT

[3]   Imada M, Fujimori A and Tokura Y 1998 *Rev. Mod. Phys.* **70** 1039
[4]   Kuwamoto H, Honig J M and Appel J 1980 *Phys. Rev.* B **22** 2626
[5]   Limelette P, Georges A, Jérome D, Wzietek P, Metcalf P and Honig J M 2003 *Science* **302** 89
[6]   Luo Q, Guo Q and Wang E G 2004 *Appl. Phys. Lett.* **84** 2337
[7]   Grygiel C, Simon Ch, Mercey B, Prellier W, Frésard R and Limelette P 2007 *Appl. Phys. Lett.* **91** 262103
[8]   Allimi B S, Aindow M and Alpay S P 2008 *Appl. Phys. Lett.* **93** 112109
[9]   Schwingenschlögl U, Frésard R and Eyert V 2009 *Surf. Sci.* **603** L19
[10] Schwingenschlögl U and Schuster C 2009 *Chem. Phys. Lett.* **467** 354
[11] Klein A, Tiefenbacher S, Eyert V, Pettenkofer C and Jaegermann W 2001 *Phys. Rev.* B **64** 205416
[12] Sferco S, Blaha P and Schwarz K 2007 *Phys. Rev.* B **76** 075428
[13] Schwingenschlögl U and Schuster C 2007 *Chem. Phys. Lett.* **449** 126
[14] Gemming S and Seifert G 2006 *Acta Mat.* **54** 4299
[15] Schwingenschlögl U and Schuster C 2008 *Europhys. Lett.* **81** 17007
[16] Eyert V 2000 *Int. J. Quantum Chem.* **77** 1007
[17] Eyert V 2007 *The Augmented Spherical Wave Method – A Comprehensive Treatment (Lecture Notes in Physics* vol 719) (Berlin: Springer)
[18] Eyert V and Höck K-H 1998 *Phys. Rev.* B **57** 12727
[19] Eyert V 1996 *J. Comp. Phys.* **124** 271
[20] Blöchl P E, Jepsen O and Andersen O K 1994 *Phys. Rev.* B **49** 16223
[21] Schwingenschlögl U, Eyert V and Eckern U 2003 *Europhys. Lett.* **61** 361
      Schwingenschlögl U, Eyert V and Eckern U 2003 *Europhys. Lett.* **64** 682
[22] Schwingenschlögl U and Eyert V 2004 *Ann. Phys., LPZ.* **13** 475
[23] Dernier P D 1970 *J. Phys. Chem. Solids* **31** 2569
[24] Kresse G, Surnev S, Schoiswohl J and Netzer F P 2004 *Surf. Sci.* **555** 118
[25] Held K, Keller G, Eyert V, Vollhardt D and Anisimov V I 2001 *Phys. Rev. Lett.* **86** 5345
[26] Keller G, Held K, Eyert V, Vollhardt D and Anisimov V I 2004 *Phys. Rev.* B **70** 205116
[27] Pentcheva R and Pickett W E 2008 *Phys. Rev.* B **78** 205106
[28] Schwingenschlögl U and Schuster C 2009 *Europhys. Lett.* **86** 27005
      Schwingenschlögl U and Schuster C 2009 *Chem. Phys. Lett.* **467** 354
[29] Grygiel C, Pautrat A, Prellier W and Mercey B 2008 *Europhys. Lett.* **84** 47003
[30] Fu C L, Ohnishi S, Wimmer E and Freeman A J 1984 *Phys. Rev. Lett.* **53** 675
[31] Lee J I, Fu C L and Freeman A J 1986 *J. Magn. Magn. Mater.* **62** 93
[32] Eyert V, Schwingenschlögl U and Eckern U 2005 *Europhys. Lett.* **70** 782