Covalent bonding and hybridization effects in the corundum-type transition-metal oxides V$_2$O$_3$ and Ti$_2$O$_3$

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Abstract. – The electronic structure of the corundum-type transition-metal oxides V$_2$O$_3$ and Ti$_2$O$_3$ is studied by means of the augmented spherical wave method, based on density-functional theory and the local density approximation. Comparing the results for the vanadate and the titanate allows us to understand the peculiar shape of the metal 3$d$ $a_{1g}$ density of states, which is present in both compounds. The $a_{1g}$ states are subject to pronounced bonding-antibonding splitting due to metal-metal overlap along the $c$-axis of the corundum structure. However, the corresponding partial density of states is strongly asymmetric with considerably more weight on the high energy branch. We argue that this asymmetry is due to an unexpected broadening of the bonding $a_{1g}$ states, which is caused by hybridization with the $e^\pi_g$ bands. In contrast, the antibonding $a_{1g}$ states display no such hybridization and form a sharp peak. Our results shed new light on the role of the $a_{1g}$ orbitals for the metal-insulator transitions of V$_2$O$_3$. In particular, due to $a_{1g}$-$e^\pi_g$ hybridization, an interpretation in terms of molecular orbital singlet states on the metal-metal pairs along the $c$-axis is not an adequate description.

Based on the electronic level scheme of Castellani et al. [1], V$_2$O$_3$ was studied extensively as the canonical Mott–Hubbard system. Due to octahedral coordination of the metal sites, the V 3$d$ states are split into lower $t_{2g}$ and higher $e^\pi_g$ levels. Trigonal lattice symmetry leads to further separation of the former into $a_{1g}$ and $e^\pi_g$ states. Covalent V-V bonding along the hexagonal $c$-axis of the corundum structure results in bonding and antibonding $a_{1g}$ molecular orbitals, which sort of bracket the $e^\pi_g$ levels. Electronic structure calculations confirmed the gross features of this scheme with $t_{2g}$ states close to the Fermi level [2]. As proposed by Castellani et al., the bonding $a_{1g}$ states are fully occupied, whereas the antibonding states shift to higher energies. This leaves one electron per V atom in the twofold degenerate $e^\pi_g$ orbital and leads to an $S = 1/2$ state, suggesting to use the one-band Hubbard model at half filling for describing the metal-insulator transitions (MITs) of V$_2$O$_3$. The stoichiometric compound undergoes an MIT at 168 K, leading from a paramagnetic metallic (PM) to an antiferromagnetic insulating (AFI) phase; on doping with Cr or Al a paramagnetic insulating (PI) phase is found [3, 4].

The model by Castellani et al. has been called into question by polarized x-ray absorption spectroscopy experiments, which point at an $S = 1$ spin state of the metal atoms [5]. The

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lowest excited states miss pure $e^\pi_g$ symmetry but reveal remarkable $a_{1g}$ admixtures calling for a treatment beyond the one-band Hubbard model. LDA+U calculations explain the peculiar antiferromagnetic order at low temperatures and point at an $S = 1$ configuration [6], which also results from the model calculations by Mila et al. [7]. Starting with the assumption of strong covalent bonding in the V-V pairs parallel to the $c$-axis, these authors suppose the intersite $a_{1g}$ hopping matrix element to dominate. However, a recent study of the hopping processes in V$_2$O$_3$ found relevant matrix elements also between second, third, and fourth nearest neighbours [8]. LDA band structures show only minor response to the structural modifications occurring at the phase transitions of V$_2$O$_3$, whereas a correct description of the PM-PI transition has been obtained by a combination of LDA calculations with the dynamical mean field theory (DMFT) [9,10]. Nonetheless, confirming an early suggestion by Dernier [11] we have recently demonstrated that considering the rearrangements of the metal-metal overlap perpendicular to the hexagonal $c$-axis is important for understanding the MITs of V$_2$O$_3$ [12–14].

Ti$_2$O$_3$ is isostructural to corundum V$_2$O$_3$ and undergoes a gradual MIT without symmetry breaking lattice distortion between 400 K and 600 K. In contrast to V$_2$O$_3$, its low temperature insulating state is non-magnetic. As in V$_2$O$_3$, the $a_{1g}$ states mediate strong bonding between Ti-Ti pairs in face-sharing octahedra parallel to the hexagonal $c$-axis, leading to bonding and antibonding $a_{1g}$ bands bracketing the $e^\pi_g$ states. An insulating energy gap is expected between the bonding $a_{1g}$ and $e^\pi_g$ states [15]. According to this picture increase of the $c/a$ ratio of the corundum lattice constants with increasing temperature reduces the $a_{1g}$ band splitting and promotes a collapse of the energy gap. Band structure calculations by Mattheiss [16] revealed a partially filled $t_{2g}$ complex of overlapping $a_{1g}$ and $e^\pi_g$ bands at the Fermi level. Decreasing the $c/a$ ratio reduces but does not eliminate the $a_{1g}$-$e^\pi_g$ band overlap. To open the gap, an unphysically small Ti-Ti distance of 2.2 Å parallel to the $c$-axis is required, which precludes a simple band explanation of the MIT. Recent cluster LDA+DMFT calculations assuming moderate Coulomb interactions among the $t_{2g}$ orbitals reproduced the insulating state [17].

In this Letter we report on electronic structure calculations for both V$_2$O$_3$ and Ti$_2$O$_3$ using the respective room-temperature crystal structure data. Our calculations i) result in a new interpretation of the bonding and antibonding $a_{1g}$ states and ii) reveal striking differences in the hybridizations of the V 3$d$ $e^\pi_g$ bands with the bonding and antibonding $a_{1g}$ states, respectively. While hybridization of the $e^\pi_g$ bands with the bonding $a_{1g}$ states is rather strong, leading to significant broadening of these bands, the antibonding states are of pure $a_{1g}$ character.

The present LDA band structure calculations are based on the scalar-relativistic augmented spherical wave (ASW) method [18,19]. Crystallographic data reported by Dernier for V$_2$O$_3$ [11] and by Rice and Robinson for Ti$_2$O$_3$ [20] were used. To model the crystal potential in the large voids of the open crystal structures, additional augmentation spheres were included. Optimal augmentation sphere positions and radii of all spheres were automatically generated by the sphere geometry optimization (SGO) algorithm [21]. The basis sets comprised V/Ti 4$s$, 4$p$, 3$d$, and O 2$s$, 2$p$ orbitals as well as states of the additional augmentation spheres. Brillouin zone integrations were performed using up to 2480 k-points within the irreducible wedge.

As is typical for transition-metal chalcogenides with octahedral coordination, V$_2$O$_3$ shows three groups of bands in the vicinity of the Fermi level, extending from $-8.8$ eV to $-3.9$ eV, from $-1.1$ eV to $1.5$ eV, and from $1.9$ eV to $3.8$ eV, see Fig. 4. They originate from O 2$p$, V 3$d$ $t_{2g}$, and V 3$d$ $e^\pi_g$ states, respectively. The right hand side of Fig. 4 shows the V 3$d$ density of states (DOS) for the latter two groups of bands separated into its symmetry components.
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Fig. 1 – V$_2$O$_3$: weighted electronic bands and partial V 3d DOS. The length of the bars in the band structure indicates V 3d $a_{1g}$ contributions.

$a_{1g}$, $e_g^\pi$, and $e_g^\sigma$. V-O hybridization results in additional O 2p admixtures in the energy range shown, which are stronger for the $\sigma$-bonding $e_g^\sigma$ states. Octahedral coordination of the metal atoms leads to almost perfect energetical separation of the $t_{2g}$ and $e_g$ groups of bands. Small contributions of $t_{2g}$ states in the $e_g^\sigma$ energy range above 1.9 eV are mainly due to the V-V anti-dimerization along the c-axis, which shifts the metal atoms off the centers of their oxygen octahedra and results in a metal-metal distance much larger than the ideal value of 1/6 of the c lattice constant.

The band structure of the $t_{2g}$ and $e_g$ groups of bands is displayed on the left hand side of Fig. 1 where the length of the bars added to the bands is proportional to the respective $a_{1g}$ contribution. Hence, bands without bars are of $e_g^\pi$ and $e_g^\sigma$ character, respectively, in the lower and upper group shown. The band structure refers to the non-primitive hexagonal representation of the trigonal unit cell. While the dispersion of the $e_g^\pi$ bands is rather isotropic, the $a_{1g}$ bands have an increased dispersion along the line $\Gamma$-A. Perpendicular to this line, i.e. along the paths $\Gamma$-M-K-$\Gamma$ and A-L-H-A, the $a_{1g}$ states are found mainly at the lower and upper boarder of the band complex at the Fermi level. This holds especially for the bands above 1 eV in the $\Gamma$-M-K-$\Gamma$ plane, which are well separated from the lower lying bands.

The pronounced one-dimensionality of the $a_{1g}$ bands leads to the characteristic shape of the $a_{1g}$ partial DOS. It suggests to interprete the peak at $-0.9$ eV and the double-peak at $0.8/1.0$ eV, respectively, as the bonding and antibonding states resulting from the V-V overlap across the octahedral faces. However, the weights of these peaks are far from equal but have a ratio of about 1:3, contradicting expectations based on a molecular orbital point of view. Due to the reduced weight of the lower $a_{1g}$ peak the occupation of the twofold degenerate $e_g^\sigma$ states is larger than one, explaining the experimental findings of Park et al. [5].

In order to understand these puzzling results we turn to titanium sesquioxide, which has the same octahedral coordination of the transition-metal sites with octahedra neighbouring
along the c-axis interlinked via faces. The band structure and the partial densities of states of Ti$_2$O$_3$ are displayed in Fig. 2 in the representation already used for V$_2$O$_3$ in Fig. 1. From the structural similarity of the two compounds we expect the same gross features of their electronic structures. Indeed, we obtain for Ti$_2$O$_3$ three groups of bands in the vicinity of the Fermi level, extending from $-9.0\,\text{eV}$ to $-4.5\,\text{eV}$ (O 2$p$), $-0.9\,\text{eV}$ to $2.3\,\text{eV}$ (Ti 3$d$ $t_2g$), and $2.4\,\text{eV}$ to $4.1\,\text{eV}$ (Ti 3$d$ $e_g^\pi$). Additional Ti 4$s$ bands are found at energies higher than $3.9\,\text{eV}$. These results agree well with the findings of Mattheiss [16].

The symmetry components of the Ti 3$d$ DOS (right hand side of Fig. 2) confirm the energetical separation of the $t_{2g}$ and $e_g^\sigma$ states as well as the $t_{2g}$ admixture to the bands above $2.4\,\text{eV}$ due to the metal-metal anti-dimerization along the c-axis. In the band structure shown on the left hand side of Fig. 2 we distinguish the isotropically dispersing $e_g^\pi$ bands from the $a_{1g}$ states, which are highlighted by the bars attached to each band and display a rather one-dimensional behaviour. The latter causes the characteristic shape of the $a_{1g}$ partial DOS with the pronounced peaks at $-0.7\,\text{eV}$ and $1.7\,\text{eV}$, which as before might be attributed to bonding-antibonding splitting due to metal-metal overlap along the c-axis. Yet, we are again faced with a decreased weight of the low-energy peak leading to the finite $e_g^\sigma$ occupation.

While the results for V$_2$O$_3$ and Ti$_2$O$_3$ are quite similar in general, we observe distinct differences at a closer look. They might give a first clue to the problem of the unequal weights of the $a_{1g}$ peaks and pave the way for a better understanding of the role of these electronic states. To be specific, we point to the small gap at $1.2\,\text{eV}$ in the partial DOS of the titanate, separating the peak at $1.7\,\text{eV}$ from the lower lying bands. Such a gap is not observed for the vanadate. Since the $a_{1g}$ partial densities of states both below and above $1.2\,\text{eV}$ integrate to about one electron each, it is tempting to interpret the bands above this gap as antibonding and the whole of the $a_{1g}$ bands between $-1\,\text{eV}$ and $1.2\,\text{eV}$ as bonding. If this point of view were correct, the bonding $a_{1g}$ states would thus extend over a very broad energy interval of

![Fig. 2 - Ti$_2$O$_3$: weighted electronic bands and partial Ti 3$d$ DOS. The length of the bars in the band structure indicates Ti 3$d$ $a_{1g}$ contributions.](image-url)
more than 2 eV.

This quite unusual situation should be related to the second observation growing out of the comparison of Figs. 1 and 2, namely the conspicuous downshift of the upper edge of the $e_g^\pi$ states. While in the vanadate these bands share edges with the whole of the $a_{1g}$ states, there exists only a tiny contribution at energies above 1.2 eV in the titanate. In contrast, the $e_g^\pi$ partial DOS displays a very sharp cutoff at this energy. Obviously, the $e_g^\pi$ states are found only in the energy region of the bonding but not of the antibonding $a_{1g}$ states. Going one step further, we infer from the similar shape of both partial densities of states below 1.2 eV, in particular from the common peaks near −0.7 eV, 0.2 eV, 0.5 eV, and 1.0 eV, a considerable amount of $a_{1g}$-$e_g^\pi$ mixing. We thus attribute the large band width of the low-energy $a_{1g}$ states to the strong $a_{1g}$-$e_g^\pi$ hybridization. Since the broadening is of similar size as the bonding-antibonding splitting of the $a_{1g}$ band, we end up with the complex situation observed for the vanadate.

In order to “prove” the just sketched scenario, we turn in the last step to another set of calculations for V$_2$O$_3$ with a hypothetical crystal structure. In this structure the V-V bond length along the $c$-axis has been reduced from 2.70 Å to 2.51 Å, while the symmetry of the corundum structure, the lattice constants, and the oxygen positions were retained. As a result of these changes, hypothetical V$_2$O$_3$ is characterized by a short intrapair V-V distance, hence, by increased intrapair bonding. Eventually, this will cause a stronger bonding-antibonding splitting of the $a_{1g}$ states. As a consequence, we expect a much clearer separation of these states as compared to the results given in Fig. 1. The band shifts occurring on going from the real to the artificial structure of V$_3$O$_3$ will thus allow us to make a clear distinction between bonding and antibonding $a_{1g}$ states for this material.

The calculated results for the hypothetical V$_2$O$_3$ structure are displayed in Fig. 3 using the same representation of the band structure and V 3d DOS as in Figs. 1 and 2. While the
V 3d $e_g^\pi$ DOS of artificial V$_2$O$_3$ still resembles the results for real V$_2$O$_3$, we observe indeed distinct modifications especially for the $a_{1g}$ DOS. The peak at $-0.8$ eV in Fig. [1] shifts to lower energies, and the peak at 1.0 eV (having a pronounced shoulder at 0.7 eV, see Fig. [1]) splits into two peaks at 0.8 eV and 1.3 eV leaving a gap at about 1.0 eV. At the same time the upper edge of the $e_g^\pi$ states experiences a strong downshift and displays a sharp cutoff. Eventually, the band structures and densities of states of artificial V$_2$O$_3$ become more similar to those of Ti$_2$O$_3$. From the differences between real and artificial V$_2$O$_3$ we thus associate the $a_{1g}$ peak around 1.3 eV with the antibonding states due to intrapair bonding. At lower energies, strong $a_{1g}$-$e_g^\pi$ hybridization leads to a considerable broadening of the bonding $a_{1g}$ branch, which extends from $-1.2$ eV to 1.0 eV. Note that both the bonding and antibonding states integrate to equal weights. Transferring these findings to real V$_2$O$_3$, we conclude that the $a_{1g}$ peak at 1.0 eV in Fig. [1] represents the antibonding states, whereas the region of bonding states extends from $-1.1$ eV to $\approx 0.9$ eV and even includes the shoulder at 0.7 eV.

In general, our findings agree well with the results of the recent LDA+U calculations by Ezhov et al. as well as Elfimov et al. for antiferromagnetic and assumed ferromagnetic V$_2$O$_3$ [6,8]. The main difference between both approaches concerns the relative downshift of the $e_g^\pi$ states, which eventually opens the insulating gap observed for the AFI phase. However, the LDA+U calculations likewise result in a finite $a_{1g}$-$e_g^\pi$ hybridization for the bonding $a_{1g}$ states whereas the $e_g^\pi$ admixture to the antibonding $a_{1g}$ states vanishes. Hence, while the LDA+U treatment leads to a somewhat changed scenario the basic mechanisms are still well described by the LDA calculations.

Still, it remains an open question why the bonding $a_{1g}$ states are subject to hybridization with the $e_g^\pi$ states, while the antibonding states retain their pure band character. Of course, it is tempting to relate this finding to the aforementioned metal-metal anti-dimerization, which shifts the metal atoms along the c-axis off the center of their respective oxygen octahedra. Since the displacement is parallel to the principal axis of the $a_{1g}$ orbitals, the resulting increase in d-p overlap mainly affects these states and is much less pronounced for the $e_g^\sigma$ bands. The $a_{1g}$ states are thus found at slightly elevated energy, the difference of the centers of gravity amounting to $\approx 0.3$ eV for V$_2$O$_3$ [10]. As a consequence, the lower bonding part of the $a_{1g}$ bands experiences more overlap with the $e_g^\pi$ states than the high-energy antibonding $a_{1g}$ states.

Nevertheless, a more convincing argument is based on the symmetry of the electronic orbitals involved, as well as the much different degree of overlap of the $t_{2g}$ orbitals within the c-axis pairs. As a matter of fact, the $e_g^\pi$ orbitals arise as linear combinations of all five d states, except for the d$_{3z^2-r^2}$ states which are identical to the $a_{1g}$ states. In addition, the overlap of the $e_g^\sigma$ orbitals within the vanadium pairs along the c-axis is close to negligible. As a consequence, these states are symmetric with respect to reflection about the midplane between the two atoms. This is different for the $a_{1g}$ states, which do overlap along the c-axis this leading to the bonding and antibonding combinations. Since the bonding and antibonding $a_{1g}$ states are even and odd functions with respect to reflections, only the former may hybridize with the $e_g^\pi$ orbitals, whereas the latter do not overlap with these states.

In conclusion, the electronic structure of the corundum-type sesquioxides V$_2$O$_3$ and Ti$_2$O$_3$ is strongly influenced by a complex interplay of i) the formation of bonding and antibonding states arising from overlap of the metal 3d $a_{1g}$ states across octahedral faces and ii) strong hybridization of the bonding but not the antibonding $a_{1g}$ bands with the $e_g^\pi$ states. The hybridization disturbs the formation of molecular orbital singlet states by the $a_{1g}$ orbitals of the vertical V-V pairs. Therefore, the occupation of the $e_g^\pi$ bands is increased this explaining the recently observed $S = 1$ configuration. As a consequence, failure of the model by Castellani et al. is mainly due to hybridization effects and not purely a consequence of the energy lowering of the $e_g^\pi$ states. In addition, since for symmetry reasons the $a_{1g}$-$e_g^\pi$ hybridization affects only
the bonding $a_{1g}$ states, the corresponding partial DOS assumes a strongly asymmetric shape. The observed strong 3D-coupling of the $a_{1g}$ orbitals appears to be a primal feature of the electronic structure of these sesquioxides and therefore is of special importance for models dealing with the MITs in this compound. The findings for V$_2$O$_3$ strongly differ from those for VO$_2$ and Ti$_4$O$_7$, where hybridization between the $d_{∥}$ states, which are responsible for metal-metal overlap, and the $e^π_σ$ states is suppressed and thus allows for a Peierls-type mechanism of the MIT [22, 23].

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REFERENCES

[1] Castellani C., Natoli C. R. and Ranninger J., Phys. Rev. B, 18 (1978) 4945; 18 (1978) 4967; 18 (1978) 5001.
[2] Mattheiss L. F., J. Phys.: Condens. Matter, 6 (1994) 6477.
[3] McWhan D. B., Remeika J. P., Rice T. M., Brinkman W. F., Maita J. P. and Menth A., Phys. Rev. Lett., 27 (1971) 941.
[4] McWhan D. B., Menth A., Remeika J. P., Brinkman W. F. and Rice T. M., Phys. Rev. B, 7 (1973) 1920.
[5] Park J.-H., Tjeng L. H., Tanaka A., Allen J. W., Chen C. T., Metcalf P., Honig J. M., de Groot F. M. and Sawatzky G. A., Phys. Rev. B, 61 (2000) 11506.
[6] Ezhov S. Yu., Anisimov V. I., Khomskii D. I. and Sawatzky G. A., Phys. Rev. Lett., 83 (1999) 4136.
[7] Mila F., Shina R., Zhang F.-C., Joshi A., Ma M., Anisimov V. and Rice T. M., Phys. Rev. Lett., 85 (2000) 1714.
[8] Elfimov I. S., Saha-Dasgupta T. and Korotin M. A., Phys. Rev. B, 68 (2003) 113105.
[9] Held K., Keller G., Eyert V., Vollhardt D. and Anisimov V. I., Phys. Rev. Lett., 86 (2001) 5345.
[10] Keller G., Held K., Eyert V., Vollhardt D. and Anisimov V. I., Phys. Rev. B, 70 (2004) 205116.
[11] Dernier P. D., J. Chem. Phys. Solids, 31 (1970) 2569.
[12] Schwingenschl"ogl U., Eyert V. and Eckern U., Europhys. Lett., 61 (2003) 361.
[13] Schwingenschl"ogl U., Eyert V. and Eckern U., Europhys. Lett., 64 (2003) 682.
[14] Schwingenschl"ogl U. and Eyert V., Ann. Phys. (Leipzig), 13 (2004) 475.
[15] Van Zandt L. L., Honig J. M. and Goodenough J. B., J. Appl. Phys., 39 (1968) 594.
[16] Mattheiss L. F., J. Phys.: Condens. Matter, 8 (1996) 5087.
[17] Poteryaev A. I., Lichtenstein A. I. and Kotliar G., Phys. Rev. Lett., 93 (2004) 086401.
[18] Williams A. R., K"ubler J. and Gelatt C. D. jr., Phys. Rev. B, 19 (1979) 6094.
[19] Eyert V., Int. J. Quant. Chem., 77 (2000) 1007.
[20] Rice C. E. and Robinson W. R., Acta Crystallogr. B, 53 (1977) 1342.
[21] Eyert V. and H"ock K.-H., Phys. Rev. B, 57 (1998) 12727.
[22] Eyert V., Ann. Phys. (Leipzig), 11 (2002) 650.
[23] Eyert V., Schwingenschl"ogl U., and Eckern U., Chem. Phys. Lett., 390 (2004) 151.