Role of c-axis pairs in V$_2$O$_3$ from the band-structure point of view.

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The common interpretation of the LDA band structure of V$_2$O$_3$ is that the apparent splitting of the $a_{1g}$ band into a low intensity structure deep below the Fermi energy and a high intensity feature above it, is due to the bonding-antibonding coupling of the vertical V-V pair. Using tight-binding fitting to—as well as first-principles NMTO downfolding of—the spin-up LDA+U $a_{1g}$ band, we show that there are other hopping integrals which are equally important for the band shape as the integral for hopping between the partners of the pair.

A few years ago, Park et al. reexamined the so-called spin 1/2 model for V$_2$O$_3$ [1]. Based on polarization dependent x-ray absorption measurements they showed that, for all phases, the vanadium 3+ ion ($d^2$) is in the spin 1 state. They also demonstrated that this state is a mixture of $e_g^2e_g^\pi$ and $e_g^2a_{1g}$ configurations, with the former having the larger weight, especially at low temperatures. Recall, that the $t_{2g}$ orbitals, which are $p_{d\sigma}$ anti-bonding with the O $p$ orbitals on the surrounding octahedron, lie below the $p_{d\pi}$ anti-bonding $e_g$ orbitals and are split by a trigonal distortion into low-lying, doubly degenerate $e_g^\pi$ orbitals and a higher-lying $a_{1g}$ orbital. The picture presented by Park et al. is hardly consistent with the classical vertical-pair assumption that the bonding-antibonding splitting of the $a_{1g}$ orbitals of the V-V pair places the energy of the bonding orbital well below that of the $e_g^\sigma$ orbitals [2] [3]. This is the assumption which 25 years ago led Castellani et al. to suggest the spin 1/2 model where for the V-V pair two electrons fill the bonding $a_{1g}$ orbital and the two remaining electrons 1/4-fill the four $e_g^\pi$ orbitals [4]. It is now generally recognized that the spin 1/2 model is incorrect. Nevertheless, the vertical pair remains a popular starting point for current attempts to calculate the electronic structure of V$_2$O$_3$ [5] [6] [7]. A comprehensive review of the latest experimental and theoretical results in this field can be found in a recent paper by Di Matteo, Perkins and Natoli [8].

In the present paper we study the dispersion of the $a_{1g}$ band obtained from a modern LDA+U calculation by performing a tight-binding analysis. Our motivation for doing this is to obtain information regarding the smallest cluster that one can use in the model calculations while still preserving the most important aspects of the band structure. In spite of the fact that some literature exists providing the qualitative hint concerning this, we considered it to be rather important to check this with more recent methodology (e.g. the downfolding technique) providing the quantitative estimates. Note that, although the spatial orientation of an $a_{1g}$ orbital is actually in favour of a molecular-like picture, our analysis shows that there are other hopping integrals which are equally important for description of the main features of the band structure as the hopping integral between the partners of the $c$ axis pair ($t_1$). Though these inter-pair hopping integrals are smaller than $t_1$, the contribution is proportional to the number of neighbours and that makes them rather significant.

Since we are interested in understanding the relative importance of the hopping between pairs and non-pairs, we consider the band structure of ferromagnetic V$_2$O$_3$ in the high-temperature corundum structure. Although this phase does not exist in nature, it can provide a good estimate of an upper bound for the hopping integrals in this compound for the following reasons: First of all, comparing with antiferromagnetic phases, the ferromagnetic one has the largest band-width [10]. Secondly, the distance between the partners of a vertical pair is shorter in the corundum structure than in the low-temperature monoclinic phase [11]. Therefore the hopping integral between partners of the pair in this structure should be maximal.

In Fig.1 we show the LDA and LDA+U spin-up band structure of V$_2$O$_3$ in the energy range of the 12 $t_{2g}$ bands (4 V atoms per cell). Comparing these two pictures one can see that the LDA+U band structure calculated for $U=3$eV and $J=0.8$eV is essentially a rigid shift of the $e_g^\pi$ band down in energy and $a_{1g}$ up so that the former is above it. However, we note that as a result the mixing between $e_g^\pi$ and $a_{1g}$ bands is suppressed. Nevertheless, it is clear from Fig.1 that this mixing does not come from the hybridization between different orbitals of the atoms in the $c$-axis pair. This warns us already about the importance of the neighbours other than the partner in the pair.
FIG. 1: LDA (upper panel) and LDA+U (lower panel) spin-up band structure of ferromagnetic V$_2$O$_3$ in the corundum structure with 2 formula units per cell. The amount of $a_{1g}$ character is indicated by the width of so-called fat bands (dotted lines). We note that Γ-Z is along the direction of the vertical pair (see Fig. 3.11 in [9] and Fig. 1 in [18]). Γ=(0,0,0); Z=(1/2,1/2,1/2); L=(0,1/2,0); F=(1/2,1/2,0). The zero of energy is at Fermi energy.

The LDA+U band structure, which yields a spin 1 $e_g^\pi e_g^\pi$ state, has the advantage that, as already mentioned, the empty $a_{1g}$ band is practically separated from the full $e_g^\pi$ band. Of course, this depends on the values of the parameters U and J used in the calculations. According to Solovyev et al., the calculated value of the screened parameter U and Hund’s rule exchange J for V $3^+$ ion in LaVO$_3$ are 3eV and 0.93eV, respectively [12]. On the other hand, an empirical estimate by Marel and Sawatzky, based on gas-phase multiplet splittings of the $3d$ series, shows that in the case of V $3d$ J is about 0.74eV [13]. In the present work we use $J=0.8$eV as estimated by Tanabe and Sugano for the free V $3^+$ ion [14, 15].

Before we discuss our results we note that, the width of the $a_{1g}$ band reaches its maximum at Γ, where it is about 2eV. One might believe that this width is mainly caused by the bonding-antibonding interaction between the vanadium pairs along the c-axis, and that the interaction between pairs is weak. In the simplest such picture only two hopping parameters would be important: A large intra-pair hopping parameter, which should give the most of the bandwidth, and a smaller inter-pair hopping. This would result in a situation where the splitting of the $a_{1g}$ band at the Γ-point is primarily determined by the value of intra-pair hopping integral. However, one notices that the band splits into four almost equally separated levels.

To shed more light on this issue, we carry out a tight-binding model calculation where the hopping integrals to the first ($t_1$), second ($t_2$), third ($t_3$) and fourth ($t_4$) nearest V neighbors are taken into account (Fig. 2). Again, $t_1$ is the hopping integral between the atoms of the c-axis pair. In Fig. 3 (a) to (d) we demonstrate how each of these parameters contribute in the dispersion of $a_{1g}$ band. Namely, switching on merely the hopping parameter $t_1$ splits the atomic $a_{1g}$ level into two doubly degenerate flat bands with energy difference $2t_1$. There is no dispersion because the atoms in-between the pairs in the structure are missing. In fact, only because these atoms are missing, does one see pairs at all. Now the main dispersion is caused by the hopping parameter $t_3$ which yields a maximal splitting of $6t_3$ at the Γ-point (the number of neighbors which an electron can hop to with $t_3$ is equal to 3). The hopping parameter $t_4$ lifts the degeneracy of each of these doubly degenerate bands. Inclusion of $t_2$ makes the band asymmetric with respect to the position of the
FIG. 3: Tight-binding $a_{1g}$ bands. The zero of energy is at the center of the gap between the split bands. (a) $t_1 = -0.25\text{eV}$, $t_2 = 0$, $t_3 = 0$, $t_4 = 0$. The splitting is $2 \times t_1$ and there is no dispersion. (b) $t_1 = -0.25\text{eV}$, $t_2 = 0$, $t_3 = -0.15\text{eV}$, $t_4 = 0$. Note that the large splitting at $\Gamma$ is dominated by $t_3$ and not $t_2$. (c) $t_1 = -0.25\text{eV}$, $t_2 = 0$, $t_3 = -0.15\text{eV}$, $t_4 = 0.06\text{eV}$. A small $t_4$, but with 6 nearest neighbors, is sufficient to cause the large splitting into 4 bands seen in the LDA+U band structure. (d) $t_1 = -0.25\text{eV}$, $t_2 = -0.03\text{eV}$, $t_3 = -0.15\text{eV}$, $t_4 = -0.06\text{eV}$. To obtain the very evident asymmetry between the upper and lower pairs of bands we need a small $t_2$. This is now close to the LDA+U band structure.

Although $t_1$ is indeed larger than other hopping integrals, its influence on the bandwidth is not that large, because there is only one nearest neighbour, as compared to 3 for $t_2$, 3 for $t_3$ and 6 for $t_4$.

It is important to note that these values for the hopping parameters are not unique. For example, $t_1 = -0.5\text{eV}$, $t_2 = -0.03\text{eV}$, $t_3 = -0.1\text{eV}$ and $t_4 = -0.04\text{eV}$ would also give a small splitting at the $Z$-point, and large one at $\Gamma$ or L, as is shown in Fig.4. This has to do with the symmetry of these points. At the $Z$-point, for instance, the splitting between the upper and lower components of the $a_{1g}$ band is $2|3t_3 - t_1|$, for $t_2 = 0$. Hence, for any given value of $t_3$ there are always two values of $t_1 \sim 3t_3 \pm \delta_Z/2$ which give exactly the same splitting. Note that $t_4$ does not influence the energies at $Z$. At the L-point, on the other hand, the splitting is determined primarily by the sum of $t_1$ and $t_3$. Therefore, no set of parameters with $t_1$ greater than 0.5eV can reproduce the LDA+U band structure at this point (unless $t_3$ and $t_1$ have the opposite signs, which is "unphysical"). Comparing figures 1 and 4, one can easily see that the two sets of parameters, which give the same splitting at $Z$, will give different levels at F, and that only the set with $t_1 = -0.25 \text{eV}$ reproduces the accidental degeneracy of the two middle levels in the LDA+U. However, to reproduce the LDA+U band in such detail may not be meaningful as long as all hopping integrals beyond $t_4$ are neglected.

Although our tight-binding study has clearly demonstrated the role of the various hopping integrals for the dispersion of the $a_{1g}$ band, and although we can find parameters which fit the LDA+U $a_{1g}$ band, it is difficult to select one set of hopping integrals because, to the accuracy expected for our model, different sets can do this. The most straightforward way to resolve this problem is to use the downfolding procedure of Andersen et. al. [16]. This procedure relies on keeping in the first-principles NMTO band-structure calculation only the relevant de-
degrees of freedom, in this case the \( a_{1g} \) Wannier-like orbitals whose LDA+U spin-up bands lie in the energy range from the Fermi level to nearly 2 eV above, and integrating out the other degrees of freedom. This naturally takes into account re-normalization effects due to the integrated-out orbitals. Fourier transform of this few-orbital downfolded and symmetrically orthonormalized NMTO Hamiltonian provides the hopping matrix elements of the corresponding tight-binding Hamiltonian. This method provides a way of generating Wannier-like functions and their single-particle Hamiltonian without any fitting procedure. The detailed discussion of such calculations for \( \text{V}_2\text{O}_3 \), as well as comparisons with Hamiltonians proposed previously, will be presented elsewhere [17]. Here we only mention a technical point specific to the present application: Since the downfolding procedure takes place at a more basic level than where U is “added” to the LDA, we need to construct the potential which yields the spin-up LDA+U band structure. That potential we obtained from the LDA potential by shifting its logarithmic-derivative functions, \( \varphi'_{Rlm}(\varepsilon, s)/\varphi_{Rlm}(\varepsilon, s) \), in energy so as to reproduce the spin-up LDA+U band structure.

From this NMTO downfolding calculation we obtained the following hopping integrals: \( t_1 = -0.30 \text{eV}, t_2 = -0.02 \text{eV}, t_3 = -0.11 \text{eV}, t_4 = -0.05 \text{eV} \), which are close, although not identical to those used in Fig.3(d). As Fig.5(a) shows, the band structure obtained from these hopping integrals differs a bit from that in Fig.3(d), and from the upper four LDA+U bands in Fig.4. The reason is simply that the downfolded band structure shown in Fig.5(b), obtained by downfolding to the the four \( a_{1g} \) bands, cannot be reproduced completely with merely \( t_1, t_2, t_3, \) and \( t_4 \). Its Hamiltonian has also non-zero higher Fourier components, which is hardly surprising. The downfolding calculation thus confirms the gross values of the hopping integrals found by tight-binding fitting to the first 4 shells, but also points to the need for including longer ranged hoppings to reproduce the details.

One should keep in mind that the hopping integrals discussed above are for vanadium-centered Wannier-like orbitals and thus different from the Slater-Koster hopping integrals for atomic oxygen and vanadium orbitals obtained by Mattheiss [18]. Following Harrison one can show that the hopping integral between \( a_{1g} \) atomic orbitals on the vanadium pair is about 0.8eV [19], whereas the one in which the oxygen degrees of freedom are integrated out is much less than that. This reduction is due to the anti-bonding character of the pd\( \pi \) interaction.

We have thus demonstrated that, although the integral for hopping between the vertical pair is the largest hopping integral, it is not the single most important one for the \( a_{1g} \) bandwidth. This is so because the actual hopping integrals are not only determined by the direct V-V hoping but also evolve via intermediate O 2p orbitals. The simple picture where only the hopping parameter within the c-axis pair is important is not sufficient to describe the \( a_{1g} \) band in \( \text{V}_2\text{O}_3 \). Our calculations show that
the hopping integrals between second, third, and fourth nearest vanadium neighbors are equally important.

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