Motivated by an early experimental study of VOSeO$_3$, which suggested that it is a quasi-2D system of weakly coupled spin dimers with a small spin gap, we have investigated the electronic structure of this material via density-functional calculations. These \textit{ab initio} results indicate that the system is better thought of as an alternating spin-1/2 chain with moderate interchain interactions, an analog of (VO)$_2$P$_2$O$_7$. The potential interest of this system for studies in high magnetic field given the presumably small value of the spin gap is emphasized.

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The search for low-dimensional s=$\frac{1}{2}$ materials with a singlet-triplet gap in the spin excitation spectrum has been a very active field of research since the discovery of high $T_c$ superconducting cuprates. The original motivation came from the possible connection between spin-gap and superconductivity, an issue still intensely debated in the context of cuprates. It became clear however with the extensive investigation of spin ladders that even purely inorganic transition-metal compounds. The main difficulty there comes from the order of magnitude of the typical range of magnetic coupling in organic materials, and the first investigations have been accordingly carried out on organic systems. These systems are tricky however, and even the most extensively studied organic ladder, Cu$_2$(C$_5$H$_4$N$_2$)$_2$Cl$_4$, is still a subject of debate and controversies. The difficulties with organic systems are two-fold: the exchange paths are not directly evident on the basis of the structure, and it is in most cases impossible to grow large single crystals.

These problems are usually much easier to solve in inorganic transition-metal compounds. The main difficulty there comes from the order of magnitude of the exchange integrals - typically several hundreds of degrees Kelvin - but if the geometry is such that the exchange integrals are reduced substantially in the spirit of the Goodenough-Kanamori-Anderson rules, then the low-temperature properties are usually easier to reach. Several qualitatively different classes of behaviour have been identified so far in this family, among which are incommensurate spin-spin correlations in the spin-Peierls high-field phase of CuGeO$_3$, magnetic field-induced long-range order in TiCuCl$_3$ and KCuCl$_2$, and magnetization plateaux in SrCu$_2$(BO$_3$)$_2$ due to magnetic field-induced localization of spin-triplets. The behaviours reported so far do not exhaust the possibilities though.

In that respect, the vanadyl system VOSeO$_3$ is potentially very interesting. This compound was first investigated by Trombe \textit{et al.}, who synthetized the system, determined its structure, and measured the temperature dependence of the susceptibility. They concluded that the system consists of weakly coupled dimers, and that the residual couplings are presumably of two-dimensional character. Besides, although the susceptibility data reported by Trombe \textit{et al.} do not allow the determination of the spin gap because of a large Curie tail, the location of the maximum of the susceptibility suggests that the gap is probably in the appropriate range to be closed by a magnetic field. However, the details of the dominant interactions, their origin as well as the role of the active orbitals at the Fermi surface could not be quantitatively discussed in that work, and the conclusions are only preliminary.

In order to check the validity of this analysis, and in particular to determine whether the couplings are indeed essentially two-dimensional, we have performed an \textit{ab initio} calculation of the electronic properties of this system, followed by a tight-binding-downfolding analysis in order to define the important hopping parameters in this compound. As we shall see, the emerging picture is somewhat different, although not less interesting, than that guessed by Trombe \textit{et al.}.

In order to understand the electronic behavior of this system, an examination of the crystal structure is essential. VOSeO$_3$ crystallizes in the monoclinic space-group P2$_1$/c with lattice parameters $a = 4.0168$ Å, $b = 9.788$ Å, $c = 8.001$ Å, $\beta = 99.42^\circ$, and it contains four formula units per primitive unit cell. The vanadium ions V$^{4+}$ form square pyramids with the neighboring oxygens. Two adjacent up and down square pyramids share an edge and build dimeric [V$_2$O$_8$]$^{18-}$ units. These units form chains along the $x$ direction (see Fig. (a)) and are linked through Se atoms in the $yz$ plane as shown in Fig. (b). The vanadium atom in the square pyramid is shifted towards the apex oxygen and forms a short vanadium-oxygen bond ($d = 1.611$ Å) characteristic of a
vanadyl ion VO\(^{2+}\). The distance between two V\(^{4+}\) ions within the dimeric unit is of \(d = 3.175\AA\) while the distance between two dimeric units along \(x\) is \(d = 4.015\AA\) and along \(z\) is \(d = 4.841\AA\).

We have carried out a first-principles study based on the density-functional theory (DFT) in order to derive the electronic properties of VOSeO\(_3\). We have used the generalized gradient approximation (GGA)\(^{11}\) in order to include the non-local effects within the gradient approximation to go beyond the local density approximation (LDA). Calculations have been performed within the framework of both the full-potential linearized augmented plane wave (LAPW) method based on WIEN97\(^{12}\) code and the linearized muffin tin orbital (LMTO)\(^{13}\) method based on the Stuttgart TBLMTO-47 code. The results obtained by both methods are in agreement with each other.

In Fig. 2 we show a plot of the band structure along the symmetry path in the Brillouin zone \(\Gamma = (0, 0, 0), B = (-\pi, 0, 0), D = (-\pi, 0, \pi), Z = (0, 0, 0), \Gamma, V = (0, \pi, 0), A = (-\pi, \pi, 0)\). This system shows four narrow bands (four since the unit cell has four vanadium atoms) at the Fermi level with a bandwidth of about 0.5 eV. These bands are of vanadium 3d\(_{xy}\) character (in the local frame of reference with the \(z\) axis pointing along the axis connecting the vanadium ion and the apical oxygen of the square pyramid) with small mixing of oxygen \(p\) characters. They are separated by a gap of about 2 eV from the lower valence bands and a gap of 0.1 eV from the higher unoccupied conduction bands. The system is half-filled and the insulator behavior observed in this system should be explained by the effect of electron correlation which is not taken fully into account in the LDA or GGA calculations. Note that the dispersion along the \(x\) axis (chain direction) is small while in the \(yz\) plane the dispersion is of about 200 meV. This behavior already indicates that the important interactions in this system will be in the \(yz\) plane. We shall analyze this point in more detail in terms of an effective hamiltonian with parameterized hopping integrals.

We have employed LMTO-based downfolding\(^{14}\) and tight-binding analysis on the \textit{ab initio} results to obtain an effective few-orbital tight-binding description of this material. The downfolding method consists in deriving a few-orbital effective Hamiltonian from the full LDA or GGA Hamiltonian by downfolding the inactive orbitals in the tails of the active orbitals kept in the basis chosen to describe the low-energy physics. This process results in renormalized effective interactions between the active orbitals, \(V d_{xy}\) in the present case. By Fourier transforming the downfolded hamiltonian \(H_k \rightarrow H_R\),

\[
H_R = -\sum_{i,j} t_{ij} (c_j^+ c_i + c_i^+ c_j)
\]

one can then extract the effective hopping matrix elements \(t_{ij}\) between the vanadium ions. The comparison between downfolded-tight-binding bands and the DFT bands are shown in Fig. 3. The band dispersion of the four-band complex close to the Fermi level can be reproduced well by considering a few short-ranged hopping parameters (see Fig. 4): \(t_d\) is the intradimer hopping between two edge-sharing \(V^{4+}\) \(O_5\) pyramids and it is expected to give the largest contribution since it corresponds to a superexchange path \(V-O-V\) (\(\alpha \sim \alpha_{103^\circ}\)). Its value is essentially related to the width of the four-band set. In Fig. 4 we show the projection of the electron density on the \(zy\) plane (compare with Fig. 1(b)), where the contribution of the \(Vd_{xy}\)-Op-Vd\(_{xy}\) path to the intradimer coupling can be clearly identified.

The next important hopping integral is \(t_2\) which describes the interdimer coupling along the \(z\) direction. Other hopping parameters in the \(yz\) plane, \(t_4\), \(t_1\), \(t_3\) are smaller but non-negligible. They are responsible for the band-splitting along \(\Gamma D\) and dispersion along \(\Gamma Y\). Note that the paths described by \(t_3\) and \(t_4\) are not equivalent as can be observed in the electron density plot of Fig. 3 (compare with Fig. 1). The hopping integral along the chain direction \(t_2\) proves to be very small, which indicates that this interaction path is negligible. This is to be expected from the fact that the active \(d_{xy}\) orbital defined in the rotated local frame of reference with the \(z\) axis turned along the vanadium-apical oxygen, has very weak interaction with the apical oxygen \(p\) orbital. Still there are two more parameters \(t_v\) and \(t_s\) which are not to be neglected since they are responsible for the band splitting along the path \(\Gamma Z\) and dispersion along \(\Gamma Y\). This system shows a very similar behavior to CsV\(_2\)O\(_5\)\(^{15}\) as well as (VO)\(_2\)P\(_2\)O\(_5\)\(^{16}\) though in those cases important paths of interaction where provided through \(V^{5+}\) \(O_4\) and \(P^{5+}\) \(O_4\) tetrahedra groups respectively, which are not present in VOSeO\(_3\). Instead, Se\(^{4+}\) \(O_4\) trigonal pyramid groups contribute decisively to the interdimer interaction paths in VOSeO\(_3\). Those groups can be considered as playing the equivalent role to the tetrahedra groups in the above mentioned compounds.

A detailed comparison between the hopping parameters in VOSeO\(_3\) and CsV\(_2\)O\(_5\)\(^{13}\) confirms the similarity of their behavior (compare \(t_d\), \(t_2\), \(t_s\) with \(t_1\), \(t_3\), \(t_4\) in Ref.\(^{13}\)). There is a quantitative distinction though between both systems which is related to the band-splitting in VOSeO\(_3\) along the path \(\Gamma Z\) described by the hopping parameters \(t_v\) and \(t_s\) which is not present in CsV\(_2\)O\(_5\).

The analysis of the effective tight-binding model for VOSeO\(_3\) leads us to conclude that this system shows a coupled spin dimer behaviour with important interdimer coupling along the \(z\) direction and moderate to negligible couplings along \(y\) and \(x\). This picture provides a quantitative description of the important interactions in VOSeO\(_3\) as opposed to that of Trombe \textit{et al.}\(^{13}\) on the basis of their susceptibility data.

An estimate of the exchange integral related to the dominating interdimer interaction parameter \(t_d\) can be obtained by using the relation \(J \sim 4t_d^2/U\) where \(U\) is the effective onsite Coulomb repulsion on the vanadium site. Such an estimate is valid since the path described by \(t_d\)}
corresponds to a V-O-V superexchange path. Values of $U \sim 4-5 \text{eV}$ have been proposed for other vanadyl systems. Assuming that this value is similar for VOSeO$_3$, we get a $J \sim 5 \text{meV} \sim 55 \text{K}$ which is of the same order of magnitude as the $J$ value obtained by Trombe et al. ($J \sim 30\text{K}$) from the analysis of their susceptibility data.

We hope that the present results will motivate further experimental efforts to understand the properties of this system. It would be particularly interesting to investigate its properties under high magnetic field since its topology is \textit{a priori} different from that of other materials in which the spin gap could be closed.

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FIG. 2. Band-structure for VOSe$_3$ along the path $\Gamma$-B-D-Z-$\Gamma$-Y-E. The boxes indicate the band character in the local coordinate system.

FIG. 3. Comparison of the downfolded-tight-binding bands (solid lines) with the DFT bands (dotted lines). The tight-binding parameters (see Fig. 1) are (in eV) $t_d$ = 0.083, $t_2$ = 0.079, $t_4$ = 0.012, $t_3$ = 0.005, $t_4$ = 0.040, $t_v$ = 0.040, $t_s$ = 0.016, $e_0$ = -0.034, $t_x$ = 0.0.

FIG. 4. Projection on the $zy$ plane of the electron density for bands close to the Fermi level (compare with Fig. 1). Note the V$_{d_{xy}}$-$O$-$p$-V$_{d_{xy}}$ path contributing to the intradimer coupling in VOSeO$_3$. 