**Introduction**- Low-dimensional quantum spin systems with chain, ladder or planar geometries have attracted much attention in the last years due to their unconventional magnetic properties. Recently substantial effort has been devoted to the search for new materials with exotic topologies and novel properties. For instance, the group of Millet et al. has succeeded in synthesizing the first transition-metal-oxide-based nanotubular system Na$_2$V$_3$O$_7$. The discovery of Na$_2$V$_3$O$_7$ has introduced a new class of novel geometric structures in the field of magnetic nanostructures. The V$^{4+}$O$_5$ pyramids in Na$_2$V$_3$O$_7$ share edges and corners to form a nanotubular structure - a geometry first discovered for carbon- with Na atoms located inside and around each individual tube (see FIG. 1). The complex geometry of the compound is expected to provide non-trivial paths for the exchange interaction and hence to exhibit a non-trivial magnetic behavior. Initially this compound was predicted to be an example of a $S = 1/2$ nine-leg (or three-leg ladder) system with periodic boundary conditions along the rung direction. Using the extended Hückel method, Whangbo and Koo conjectured, on the other hand, that the tubes could be described by six mutually intersecting helical spin chains which should show a gap in the spin excitation spectra.

Unlike antiferromagnetic (AF) spin ladders with even number of legs, the behavior of odd-leg ladders is strongly influenced by topology. An odd-leg ladder with open boundary conditions in the rung direction behaves effectively as a $S = 1/2$ AF Heisenberg chain and therefore shows no gap in the spin-excitation spectrum. This situation changes dramatically when the boundary condition along the rung direction is periodic, as is the case for the spin tubes in Na$_2$V$_3$O$_7$. The introduction of periodic boundary conditions brings in an additional degree of freedom in the problem, namely the chirality, and the ground state is then four-fold degenerate with a gap to the first excited state. However, the magnetic properties of Na$_2$V$_3$O$_7$ as reported in the literature neither fit the properties of odd-leg spin tubes nor to that of helical spin chains as proposed by Whangbo and Koo since no appreciable spin gap could be detected in the susceptibility measurements. A way out of this puzzling situation has been suggested by Lüscher et al. by considering frustrated inter-ring couplings within the framework of a three-leg spin tube. While this surely provides an interesting model, its relevance for Na$_2$V$_3$O$_7$ remains yet to be examined.

Eventhough this compound has generated interest and controversy, no first-principles microscopic study has been reported so far. Our work in that respect is the first microscopic study carried out for Na$_2$V$_3$O$_7$. We have analyzed the ab-initio density functional theory (DFT) results in terms of the newly developed N-th order muffin-tin-orbital (NMTO) based downfolding technique to provide a microscopically-derived spin model for Na$_2$V$_3$O$_7$. Our results show that the appropriate description of the system is that of tubes of nine-site rings with partially frustrated, next-nearest neighbor intra-ring interactions and frustrated inter-ring interactions of weaker strength. Validity of this model is provided by the good agreement of our calculated susceptibility data with the measured data.

Ab-initio Study- Na$_2$V$_3$O$_7$ crystallizes in the trigonal space group, P31c. The unit cell contains six formula units and the lattice constants are $a = 10.89$ Å and $c = 9.54$ Å. There are three inequivalent V sites - V1, V2, V3, seven inequivalent O sites - O1-O7 and four inequivalent Na sites, Na1-Na4. Each V is surrounded by five oxygen atoms with one characteristic short V-O bond giving rise to distorted square pyramids which are connected to each other to form nanotubes with internal diameter of about 5 Å (see FIG. 2(a)). The arrangement of VO$_5$ pyramids in a single tube is better viewed in the unfolded idealized representation of the nanotube as shown in FIG. 2(b). The O1, O2 and O3 atoms, not marked in the figure, are positioned at the apex of VO$_5$ pyramids centered by V1, V2 and V3 atoms respectively, all of them pointing out of the tube. The edge sharing VO$_5$ pyramids form nine-member rings out of the basic unit V1-V2-V3, in alternating sequence of (V2-V1-V3)-(V2-V1-V3)-(V2-V1-V3) and (V3-V1-V2)-(V3-V1-V2)-(V3-V1-V2) within slices (A) and (B). Rings in slices (A) and (B) are connected to each other by the corner sharing oxygens O5 and O6 to form a nanotube oriented along the crystallographic c-direction.

The DFT band-structure in the generalized gradient approximation (GGA), calculated using the lin-
earized muffin tin orbital (LMTO) method based on
the Stuttgart TBLMTO-47 code\textsuperscript{12} and the linear aug-
mented plane wave (LAPW) method, consists of pri-
marily oxygen--\textit{p} and V--\textit{d} derived bands in the region
of interest.\textsuperscript{13} The oxygen--\textit{p} dominated bands are se-
parated by an energy gap of about 3 eV from the V--\textit{d}
dominated bands. The V--\textit{d} dominated bands span an
energy range of about 4 eV, starting from about -0.7 eV
to 3.5 eV, with the zero of energy set at the GGA Fermi
energy. The pyramidal co-ordination of oxygen atoms
surrounding the V atom, sets the V 3\textit{d} 1 components of the edge and corner-sharing VO\textsubscript{2} pyramids within a tube.

The inter-ring V-V couplings are generally stronger than V-O bonds and the x-axis pointing along the next
shortest V-O bond and the x-axis pointing along the next
shorter V-O bond). The V--\textit{xy} bands therefore appear
as essentially non-bonding set of bands extending from
about -0.7 eV to 0.4 eV around the Fermi level, with
small mixing of oxygen character. The crystal-field split
V--\textit{yz}, \textit{zx}, 3\textit{z}\textsuperscript{2} - 1 and \textit{x}\textsuperscript{2} - \textit{y}\textsuperscript{2} complexes appear in the
energy spectrum above the V--\textit{xy} complex in order of in-
creasing energy. Na-derived states lie farther high up in
energy with practically no mixing to bands close to the
Fermi energy.\textsuperscript{15}

Starting from such a density-functional input, it is a
non-trivial task to build up a low-energy model Hamil-
tonian relevant for the system. For the sake of unique-
ness, however, it is essential for such model Hamiltoni-
ans to be derived in a first principles manner containing
the essential chemistry of the material. In recent years
the \textit{N}-th-order-muffin-tin-orbital-method-based\textsuperscript{16} down-
folding technique has been successful in achieving this
goal.\textsuperscript{16} The method relies on designing energy-selective
Wannier-like effective orbitals by integrating out degrees of freedom that are not relevant - a method called down-
folding. The few-orbital Hamiltonian is then constructed
in the basis of these Wannier-like effective orbitals. Since
the degrees of freedom are integrated out, rather than
being simply ignored, the method naturally takes into
account the renormalization effect coming from orbitals
not considered explicitly. In particular, in the present
case, we integrate out all the degrees of freedom other
than V--\textit{xy} orbitals. The effective V--\textit{xy} muffin tin
orbitals (MTO’s) generated in the process contains in
its tail the integrated out \textit{O}--\textit{p} and remaining V--\textit{d}
orbitals, the weight being proportional to their mixing to
V--\textit{xy} derived bands. Fourier transform in the down-
folding V--\textit{xy} basis gives the tight-binding Hamiltonian,

\begin{equation}
H_{TB} = -\sum_{<i,j>} t_{ij} (c_i^\dagger c_j + c_j^\dagger c_i)
\end{equation}

\textit{ij} in terms of dominant
V-V effective hopping integrals, \textit{tij}, where \textit{i} and \textit{j}
denote a pair of V\textsuperscript{4+} ions.

The nearest neighbor (n.n.) V-V interactions within the
V1-V2-V3 basic unit (marked by dark green in FIG. 1(b)) proceed via the edge-sharing oxygens while the intra-ring next nearest neighbor (n.n.n.) inter-
actions proceed via corner-sharing oxygens.\textsuperscript{17} Our first-
principles-derived hopping integrals show that the edge-
sharing n.n. V-V interactions within the V1-V2-V3 basic
unit, \textit{t}1, \textit{t}2 and \textit{t}3 (see FIG. 2 and TABLE 1), are of mag-
nitude ranging from -0.14 eV to -0.18 eV. The n.n.n
corner sharing intra-ring interactions \textit{t}1\textsuperscript{\perp} and \textit{t}2\textsuperscript{\perp}
are equally strong. The inter-ring V-V couplings \textit{t}1\textsuperscript{\parallel}, \textit{t}2\textsuperscript{\parallel}
\textit{i} = 1, 2 are an order of magnitude weaker than the intra-
ring couplings. Nevertheless, we notice that the n.n.n
inter-ring interactions (\textit{t}1\textsuperscript{\perp} and \textit{t}2\textsuperscript{\perp}) are equally strong as the n.n.
inter-ring interactions (\textit{t}1\textsuperscript{\parallel} and \textit{t}2\textsuperscript{\parallel}). This
induces inter-ring frustration which, as we will see later,
could be of fundamental importance for the description
of the magnetic behavior of the system at low tempera-
tures.

This result is very different from the extended Hückel
molecular-orbital-based result of Whangbo and Koo\textsuperscript{18} which predicts that coupling via corner-sharing pyramids
is much larger than that via edge-sharing for Na\textsubscript{2}V\textsubscript{3}O\textsubscript{7}. While this conclusion is in general true for vanadate sys-

FIG. 1: (Color on-line) Crystal structure of Na\textsubscript{2}V\textsubscript{3}O\textsubscript{7}. (a) Projection on to (001) plane. V, Na and O atoms are denoted by black, blue and red balls respectively. (b) Unfolded view of the edge and corner-sharing VO\textsubscript{2} pyramids within a tube.

FIG. 2: Hopping parameters for Na\textsubscript{2}V\textsubscript{3}O\textsubscript{7} for V atoms belonging to slices (A) and (B) in FIG.1(b). For identification of V atoms belonging to slice (A) refer to FIG.1(b).

| Intra-ring | Inter-ring |
|-----------|-----------|
| t\textsubscript{1} | -0.18 |
| t\textsubscript{2} | -0.15 |
| t\textsubscript{3} | -0.14 |
| t\textsubscript{1}\textsuperscript{\perp} | -0.13 |
| t\textsubscript{2}\textsuperscript{\perp} | -0.14 |
| t\textsubscript{1}\textsuperscript{\parallel} | -0.03 |
| t\textsubscript{2}\textsuperscript{\parallel} | -0.02 |

TABLE I: Inter and intra-ring hopping integrals in eV. The next important hoppings are about 0.001 eV.
Our microscopically derived hopping integrals show that NaV$_2$O$_5$ can be described as formed by tubes consisting of frustrated weakly coupled nine-site rings with partial intra-ring frustration. The partial frustration is due to the absence of the second neighbor V1-V3 interaction in the ring which is neither corner-sharing nor edge-sharing, rather it is decoupled by the intervening V2(O$_5$) pyramid.

**Susceptibility** - The exchange integral, J, can be expressed in general as a sum of antiferromagnetic and ferromagnetic contributions $J = J^{AF} + J^{FM}$. In the strongly correlated limit, typically valid for transition metal oxides, the antiferromagnetic contributions are related to the hopping integrals, $t_i$, by using a perturbative approach as $J^{AF} = 4t_i^2/(U-V_{\text{inter}})$, where $t_i$ corresponds to hopping via various V-O-V superexchange paths and $U$ and $V_{\text{inter}}$ are the on-site and intersite Coulomb interactions respectively. In the absence of a generally accepted satisfactory way of direct computation of exchange integrals, such an approximate method is a good starting point for estimates of the exchange couplings as well as the relative strengths among the various exchange integrals.\(^{21}\)

In view of our ab initio results, the underlying spin-1/2 Hamiltonian for NaV$_2$O$_5$ can be written as

$$H = J_1 \sum_{i=1}^{9} \left( \vec{S}_i \cdot \vec{S}_{i+1} + \alpha_1 \vec{S}_i \cdot \vec{S}_{i+2} \right),$$

where we neglect the small differences in between the three n.n. and two n.n.n intra-ring interactions and to a first approximation also neglect the small inter-ring couplings. $\alpha_i = J_2^i/J_1$ and we impose periodic boundary conditions $\vec{S}_{L+i} = \vec{S}_{i}$ (L=9). In this model, the n.n.n coupling is inhomogeneously distributed in the sense that $\alpha_i = 0$ for $i = 1, 4, 7$ and $\alpha_i \neq 0$ ($=\alpha'$) for $i = 2, 3, 5, 6, 8, 9$ (see left illustration in FIG. 4). For a further check of the goodness of this model we considered in addition the fully frustrated model with $J_2^i = J_2$ for all $i$ ($\alpha_i = \alpha$) (see right illustration in FIG. 4).

In FIG. 4 we present a comparison of the experimentally observed inverse magnetic susceptibility with that obtained from exact diagonalization of the above-mentioned two kinds of frustrated models, varying the parameters $J_1$ as well as $\alpha$ or $\alpha'$. We observe that only the partially frustrated model ($\alpha' \neq 0$), which is the model predicted from the ab initio calculations with $J_1$ and $J_2$ antiferromagnetically signed is able to reproduce the experimental data over the whole range of temperature. The fully frustrated model consistently shows, on the other hand, an upturn of the inverse susceptibility at lower temperatures not observed experimentally. We note here that estimates of $J_1$ and $J_2$ in terms of the downfolded $t_i$ values\(^{22}\) are within the same order of magnitude as those obtained here from the susceptibility comparison.

**FIG. 3:** (Color on-line) Various intra-ring and inter-ring overlaps of the downfolded V-xy MTO-s at two V1 and V2 sites. Plotted are the orbital shapes(constant-amplitude surfaces) with the lobes of opposite signs labeled by black(magenta) and white(cyan) at site V1(V2). (a) Edge-sharing intra-ring, nearest-neighbor V1-V2 overlap ($t_1$) (b) Corner-sharing intra-ring, second neighbor V1-V2 overlap ($t'_1$) (c) Inter-ring V1-V2 overlap ($t_{1,2}$).

**FIG. 4:** Temperature dependence of the inverse magnetic susceptibility in units of mol/emu obtained from exact diagonalization for the two frustrated models of the inset (see Eq. (1)) compared with the experimental data (filled dots).
FIG. 2) which will be important at low temperatures and degenerate spin-doublet four-fold degenerate ground state, i.e. it is a chirality-inter-ring couplings. Our though small- there are various contributions, t⊥ will generally induce a spin-gap which will scale with the inter-ring exchange coupling. On the other hand, the existence of two competing exchange integrals J⊥ and J′⊥ which induce inter-ring frustration changes this scenario completely. As argued previously, the partially frustrated nine-site ring model corresponds in the low-energy sector to a three-site ring. We can therefore consider at low temperatures a model of three-site rings with frustrated inter-ring couplings which maps the main features extracted from our ab initio calculations. The recent density matrix renormalization group study by Lüscher et al. on a tube of 3-site rings with frustrated inter-ring couplings showed that the spin gap diminishes if inter-ring frustration is present. For perfect frustration, i.e. J⊥=J′⊥, the spin gap goes exactly to zero since then we are left with an effective 1-dimensional S=1/2 Heisenberg model. Our ab initio hoppings t⊥ and t′⊥ are of the same strength what strongly points to the condition of almost complete frustration of the exchange integrals and therefore to a spin-gapless behavior as has been observed experimentally.

Finally, it is worth mentioning here that the partially frustrated nine-site ring model, is of considerable interest by itself. For α′ = 1 and large number of sites it is geometrically equivalent to the spin-1/2 diamond chain, which corresponds in the low-energy sector to a mixed spin-1 spin-1/2 chain.25,26 Our result α′ = 0.7 indicates that Na2V3O7 is close to the spin-diamond geometry.

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![Temperature dependence of the susceptibility (emu/mol) at low temperatures.](image-url)
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