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Leading interactions in the β - SrV_6O_{15} compound

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The present study shows that the electronic structure of the β - AV_6O_{15} family of compounds ($A = Sr, Ca, Na...$) is based on weakly interacting two-leg ladders, in contrast with the zig-zag chain model one could expect from their crystal structure. Spin dimer analysis, based on extended Hückel tight-binding calculations, was performed to determine the structure of the dominant transfer and magnetic interactions in the room temperature β - SrV_6O_{15} phase. Two different two-legs ladders, associated with different charge/spin orders are proposed to describe these one-dimensional β -type systems. The antiferromagnetic ladders are packed in an 'IPN' geometry and coupled to each other through weak antiferromagnetic interactions. This arrangement of the dominant interactions explains the otherwise surprising similarities of the optical conductivity and Raman spectra for the one-dimensional β -type phases and the two-dimensional α -type ones such as the well-known α' - NaV_2O_5 system.

I. INTRODUCTION

Vanadium oxides are known since the fifties but they have attracted a lot of attention in the recent years because of their exotic behavior. Their remarkable properties are due to the interplay between charge, spin and lattice degrees of freedom. One of the most famous example is the α' - NaV_2O_5 phase that undergoes a spin-Peierls transition¹ coupled to a spin ordering. This double transition has raised a large controversy in the last five years before its nature and origin could be elucidated, and before the apparent experimental contradictions could be lifted. Indeed, the ordering associated with the transition was supposed to be a charge ordering of the vanadium unpaired electron, located on each rung of this two-legs ladder system². While vanadium NMR³ and neutron diffraction⁴ experiments exhibited a large charge ordering at the transition, optical conductivity⁵ and resonant X-ray diffraction⁶ did not show much charge ordering. The controversy was lifted when ab-initio calculations⁷ showed that i) the bridging oxygens of the ladder rungs have an open-shell character, ii) there are three and not one magnetic electron per ladder rung and thus spin and charge densities are not compelled to be equal, iii) the system presents a large spin ordering (seen by spin sensitive experiments) associated with a very weak charge ordering (as observed in charge sensitive experiments).

Recently, superconductivity has been discovered in another family of vanadium bronzes, renewing the interest in low-dimensional vanadium oxides. The different phases of the β - AV_6O_{15} ($A = Li, Na, Ag, Ca, Sr, Cu$) family, also referred to as β - $A_{0.33}V_2O_5$, exhibit an one-dimensional (1D) metallic behavior at room temperature and undergo a metal to insulator phase transition at T_{MI} ⁸, associated with a charge ordering. Systems with monovalent cations (A^+) show a long-range magnetic order at $T < T_{MI}$ ⁹. In systems with divalent cations (A^{2+}),

no sign of long-range magnetic order is observed down to 2K and a spin gap appears in SrV_6O_{15} ¹⁰. The β -type phases present crystal structures with a 1D arrangement along the b direction — unlike the layered character of the α -type phases. They show six crystallographically independent vanadium atoms two-by-two distributed over different cationic sites : two V_1 atoms that form zig-zag double chains composed of edge-sharing VO_5 square-based pyramids, two V_2 atoms that form two-leg ladders composed of V_2bO_5 square-based pyramid sharing a corner with $V_{2a}O_6$ distorted octahedron, and two V_3 atoms that form zig-zag edge-sharing double chains, similar to the V_1 's, at first sights.

Some remarks should be done at this point.

First, in the β -type systems, phases with remarkable similitude of their structural arrangements, whether they are doped by mono- or divalent cations, exhibit very different magnetic properties. Ueda *et al*¹⁰ suggested that the differences in the magnetic properties are due to the different nature of the electronically dominant subsystem. The electronically dominant subsystem would be the zig-zag chains in the β - $A^+V_6O_{15}$ and ladders in β - $A^{2+}V_6O_{15}$ compounds.

Second, the α and β compounds have very different structural arrangements — the former is 2D while the latter is 1D — however their spectroscopic properties such as Raman¹¹ and optical conductivity spectra¹² show remarkable similitudes.

A simple formal charge analysis gives $A^+V_6^{(5-1/6)+}O_{15}^{2-}$ for monovalent cations and $A^{2+}V_6^{(5-1/3)+}O_{15}^{2-}$ for divalent cations. It comes a filling of either one or two $3d$ electrons for 6 vanadium atoms. This (low) filling, as well as the strongly localized character of the first row transition metal $3d$ orbitals, justify the use of a $t - J$ model on the vanadium sites to describe the low energy physics of such vanadates.

The present paper thus aims at elucidating the structure of the dominant electronic interactions in the β -type compounds within the hypothesis of a $t - J$ model. For this purpose, spin dimer analysis was performed using extended-Hückel tight-binding (EHTB) electronic structure calculations. Since β - AV_6O_{15} unit cells consist in (at least) four formula units, *i.e.* 88 atoms, this approach offers a pertinent alternative to prohibitive *ab initio* calculations. Furthermore, the EHTB method has been shown to provide reliable and expedient means to study the relative strengths of both hopping and spin exchange interactions in a wide variety of transition metal oxides¹³. Because strongly interacting spin exchange paths of a magnetic solid are determined either by the overlap between its magnetic orbitals for non-bridged interactions, or by the overlap between its magnetic orbitals and the bridging ligand orbitals for bridged interactions, a qualitative picture of both the dominant magnetic interactions and their nature (antiferromagnetic versus ferromagnetic) is reachable using EHTB, provided the knowledge of the crystal structure. In the present work, calculations have been performed using the crystallographic data reported for the β - SrV_6O_{15} compound¹⁴.

II. STRUCTURE OF THE DOMINANT INTERACTIONS

In the β -type compounds, five of the six vanadium atoms are surrounded by five nearest-neighbor (NN) oxygen atoms forming a distorted squared pyramid (V_{1a} , V_{1b} , V_{2b} , V_{3a} and V_{3b}). A sixth oxygen neighbor is found at a larger distance in the position issued from a highly distorted VO_6 octahedron (see figure 1). For the sixth vanadium atom V_{2a} , a less marked pyramidal structure is observed, with two short, two medium and two long $V - O$ bonds. Each pyramid may actually be seen as a

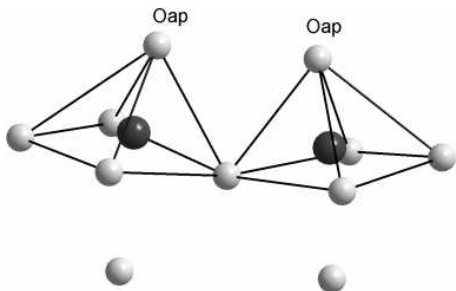


FIG. 1: Local environment of vanadium atoms in the β - AV_6O_{15} phases. Vanadium and oxygen atoms correspond to dark and light gray spheres, respectively.

vanadyl $V \equiv O_{ap}$ cation lying above a distorted square of O^{2-} anions. Indeed, the $V-O_{ap}$ distance is much smaller ($\sim 1.6\text{\AA}$) than the $V-O$ distances involving either the oxygens contained in the pyramid basal plane ($\sim 1.9\text{\AA}$ – 2.0\AA), or the sixth oxygen ($\sim 2.3\text{\AA}$). Let us note that the $V \equiv O_{ap}$ cations are not rigorously perpendicular to the

basal plane of the pyramids. The existence of an apical oxygen is crucial in these systems since the short $V-O_{ap}$ distance allows a strong delocalization to occur between these two atoms and a multiple vanadium–oxygen covalent bond to take place. This phenomenon has already been observed in the α' - NaV_2O_5 compound, in which a triple covalent/dative bond exists between the vanadium and its apical oxygen. This bond is only weakly polarized¹⁵ with an oxygen charge of about -0.5 . The experimental signature of such a strong multiple bond in the Raman spectra is a sharp peak at relatively high energy, corresponding to the bond stretching mode. This peak occurs at 969cm^{-1} for the α' - NaV_2O_5 ¹⁶, at 932cm^{-1} and 1002cm^{-1} for the CaV_2O_5 and MgV_2O_5 ¹⁷ respectively. In the β - CaV_6O_{15} ¹¹, it is seen at 978cm^{-1} , 952cm^{-1} and 877cm^{-1} for the V_3 , V_1 and V_2 vanadyl bonds. Note that the softening of the apical bond stretching mode for the V_2 atoms is due to a less marked pyramidal character of its oxygen first neighbors.

Two consequences arise from the occurrence of such a $V-O_{ap}$ multiple bond. First the formal charge of the vanadium atom is much smaller than what is usually assumed. It should be accounted as $5 - \eta - q$ instead of $5 - \eta$ where η is the number of magnetic $3d$ electrons per vanadium atom and q is the number of vanadium electrons participating to the vanadyl bond. Second and much more important, the vanadyl bond acts as a local quantification axis for the vanadium atom. As a consequence, the nature of the $3d$ magnetic orbital can be deduced from the vanadyl bond orientation : it is the d_{xy} orbital, when local axes are chosen so that z is collinear to the vanadyl bond and x and y point toward the basal plane first oxygen neighbors (see figure 2). Indeed, while the d_{z^2} , d_{xz} and d_{yz} vanadium orbitals form one σ and two π covalent/dative bonds with the apical oxygen, the d_{xy} and $d_{x^2-y^2}$ orbitals are split in agreement with the crystal field. The $d_{x^2-y^2}$ orbital is more destabilized than the d_{xy} one due to its σ -type overlap with the basal plane oxygen atoms which is larger than the π -type overlap of the d_{xy} orbital. Note that the structural difference observed for the V_{2a} local environment induces a lowering of one of the two anti-bonding π -orbitals close to the magnetic orbital energy and therefore a slightly different orientation of the V_{2a} magnetic orbital.

Focusing now on the orientation of the vanadium magnetic orbitals in the crystal structure, it becomes very simple to build the structure of the magnetic orbitals once each vanadyl bond is located. Figure 3 reports this structure for the β - SrV_6O_{15} system. The existence of two sets of vanadium atoms can be clearly seen : on one hand the V_1 and V_3 centers for which the magnetic orbitals are roughly in the (c, b) plane and on the other hand the V_2 centers for which the magnetic orbitals are nearly orthogonal to the previous ones, in the approximate $(a + c, b)$ plane.

Let us now analyze separately each type of crystallographic chain or ladder. Figure 4 reports the relative position of the magnetic orbitals for the V_2 ladder.

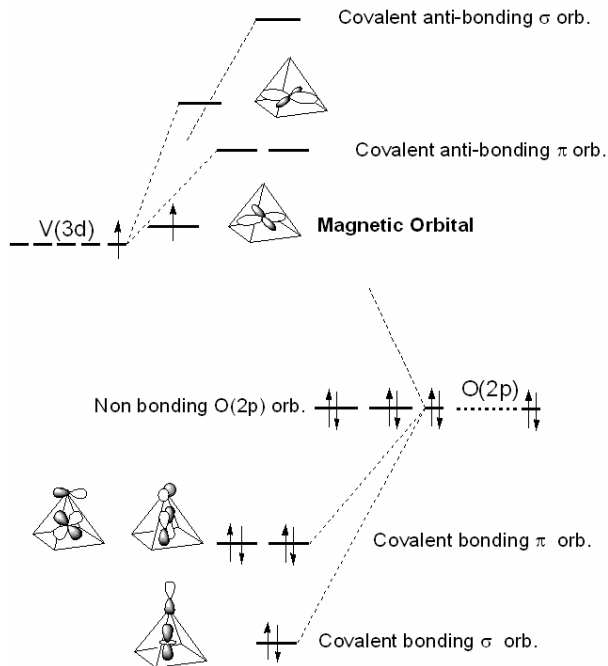


FIG. 2: Qualitative orbital interaction between the vanadium 3d orbitals and the p orbitals of the pyramid oxygens. The apical oxygen lies on the z axis, while the four oxygens of the pyramid basal plane lie on the x and y axes.

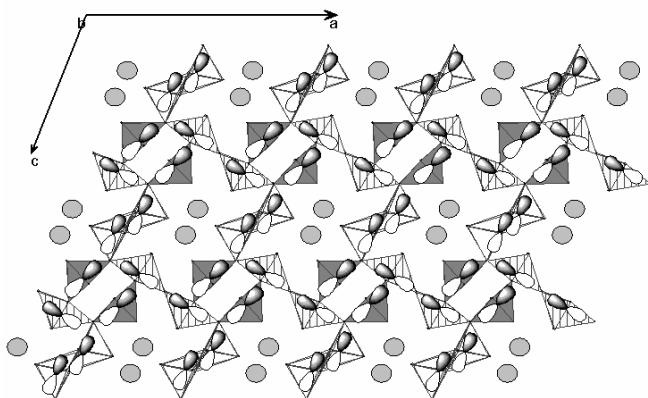


FIG. 3: Structural arrangement of the vanadium magnetic orbitals as derived both from the vanadyl bond orientation on each vanadium atom and from extended Hückel calculations. The crystal structure is represented within the (a, c) plane. The gray circles represent the counter ions, the V_2 pyramids are hatched, the V_3 are represented in white and the V_1 in gray.

Let us note that vanadyl bonds are nearly orthogonal to the figure, pointing alternatively above and below the figure plane. The bridging-oxygen p_x orbitals, along the ladder legs, and p_y orbitals along the ladder rungs strongly overlap with the neighboring V_2 magnetic orbitals. They will thus mediate both transfer and magnetic interactions. This qualitative description is con-

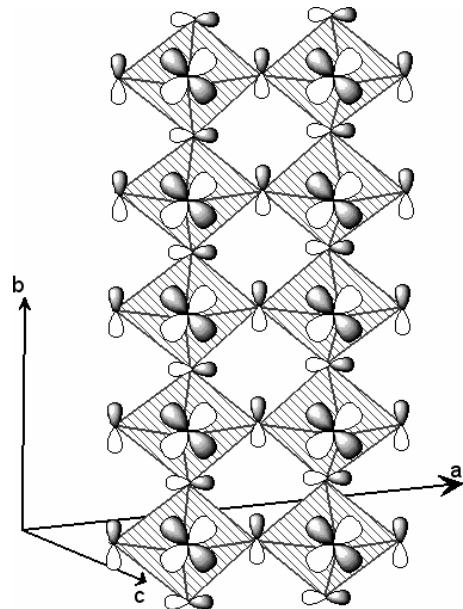


FIG. 4: Vanadium magnetic orbitals of a V_2 ladder and p orbitals of the bridging oxygen atoms mediating the interactions between the former. Note that orbital signs do not have any meaning here. The local x, y and z axes are defined as such : the z axis is in the V_2 vanadyl bond direction, the x axis is in the ladder rungs direction and the y axis along the b crystallographic direction.

firmed by spin dimer EHTB calculations since the largest spin exchange paths (*i.e.* the largest effective transfer integrals) occur between the V_2 magnetic centers, as stacked in the two-leg ladder shown in figure 4. Due to significant local distortions of the V_2 -centered pyramids, transfer integrals are larger along the ladder rungs (~ 0.31 eV) than along the ladder legs (0.17 eV and 0.21 eV). Nevertheless, both effective integrals are large enough to expect antiferromagnetic interactions between the V_2 atoms. Indeed, the effective transfer mediated through the appropriate p orbital of the bridging oxygen, can be expressed as

$$t = \pm \frac{t_{pd}^2}{\Delta_1} \quad (1)$$

and thus the bridged super-exchange mechanism comes as

$$J = -4 \frac{t_{pd}^4}{(\Delta_1)^2 U_d} - 8 \frac{t_{pd}^4}{(\Delta_1)^2 \Delta_2} \quad (2)$$

$$= -4 \frac{t^2}{U_d} - 8 \frac{t^2}{\Delta_2} \quad (3)$$

with $\Delta_1 = \delta - U_p + U_d - V_{pd}$ and $\Delta_2 = 2\delta - U_p + 2U_d - 4V_{pd}$. δ is the orbital energy difference between the vanadium magnetic orbital and the bridging oxygen p orbital, t_{pd} is the transfer integral between them, U_p and U_d are the on-site Coulomb repulsions and V_{pd} is the bi-electronic repulsion between the V and O orbitals.

Figure 5 reports the relative position of the magnetic orbital for the V_1 zig-zag chains. One sees immediately

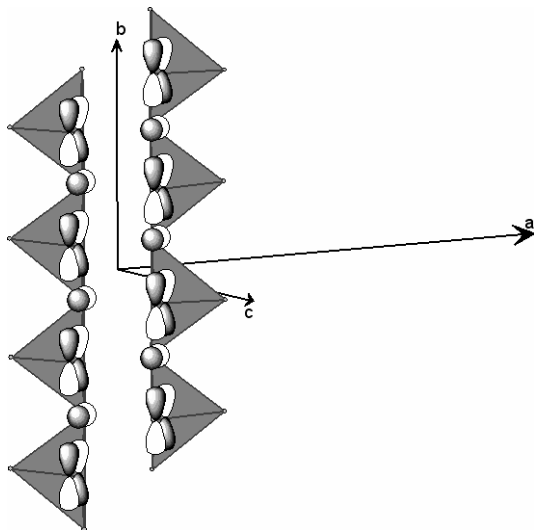


FIG. 5: Magnetic orbitals of the V_1 zig-zag chains and p orbitals of the bridging oxygen atoms involved in the mediation of the V_1 magnetic orbitals interaction. Note that the orbitals represented here are atomic orbitals and that the relative phases between them do not have any meaning. Local x , y and z axes are defined as such : z is in the vanadyl bonds direction, y is along the b crystallographic direction and x is orthogonal to the formers.

that the hopping between the magnetic orbitals of two nearest neighbors (NN) V_1 atoms is not bridged by any oxygen orbital that could mediate the interaction, and is thus restricted to its direct contribution. This direct contribution is itself expected to be very small, due to both the large distance between adjacent V_1 atoms ($\sim 3.3\text{\AA}$) and the δ character of the overlap. EHTB calculations confirm these remarks since the transfer integral between NN V_1 magnetic orbitals is found to be negligible. As far as the magnetic exchange is concerned, no super-exchange mechanism can take place between the NN V_1 atoms, for the same reasons. Therefore, the effective magnetic interaction is reduced to the direct exchange between the two vanadium atoms. It can thus be predicted to be very weak and ferromagnetic. One can clearly consider that the NN V_1 atoms do not interact. Let us now examine the coupling between second neighbor V_1 atoms. One sees on figure 5 that the associated pyramids share a corner in the b direction and that the p_x orbital of the bridging oxygen presents a large overlap with the vanadium magnetic orbitals. It can thus mediate efficiently the interaction between second neighbor V_1 atoms. EHTB calculations yield effective transfer integrals of 0.17 eV and 0.15 eV . Through-bridge super-exchange mechanism should take place and the effective exchange between second neighbor V_1 atoms can thus be expected to be reasonably large and antiferromagnetic.

Figure 6 reports the relative position of the magnetic

orbitals of both the V_1 and V_3 chains. The magnetic

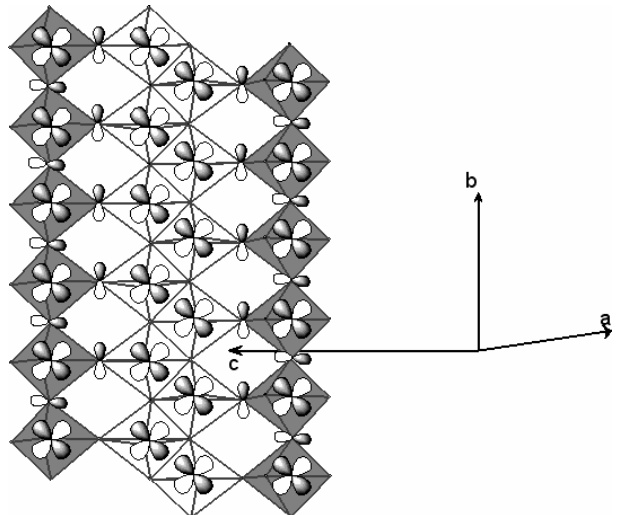


FIG. 6: Magnetic orbitals of the V_1 and V_3 chains along the b direction and p orbitals of the bridging oxygen atoms. Note that the orbitals represented here are atomic orbitals and that the relative phases between them do not have any meaning. Pyramids associated with the V_1 and V_3 atoms are represented in gray and white, respectively. Local x , y and z axes are defined as such : z is in the vanadyl bonds direction which is orthogonal to the figure plane, y is along the b crystallographic direction and x is orthogonal to the formers.

orbitals of the V_3 zig-zag chains are similar to the magnetic orbitals of the V_1 atoms since the apical axes of both sets of atoms are along the same direction. The V_3 pyramids share an edge and the interaction between the V_3 magnetic orbitals is bridged by two oxygen atoms with nearly 90° $V_3\text{-O-}V_3$ angles. It is well known that in such 90° arrangements, the contribution of the bridging-oxygen p orbitals is destructive and that the interactions between the vanadium magnetic orbitals are restricted to the direct transfer and exchange integrals. These interactions are thus weak due to the large distance between two NN vanadium atoms ($\sim 3.0\text{\AA}$). Indeed, EHTB calculations yield effective transfers between nearest neighbor V_3 atoms of the order of $\simeq 0.05\text{ eV}$ (see Appendix for the exact values of the four crystallographically different $V_3\text{-}V_3$ transfer integrals). As far as the effective exchange is concerned, one can expect it to be both weak (of the order of a few tenth of meV or smaller) and ferromagnetic — the direct exchange is always ferromagnetic in nature. Let us now examine the second neighbor $V_3\text{-}V_3$ interactions. The associated pyramids share a corner along the b direction and the p_x orbital of the oxygen atom (not shown on figure 6) can efficiently mediate the interactions between two vanadium atoms. EHTB calculations yield transfer integrals of 0.14 eV . Through-bridge super-exchange mechanism takes place via the oxygens p_x orbitals and the effective exchange between second neighbors V_3 atoms should thus be reasonably large (hundreds of meV) and antiferromagnetic.

It is clear from figure 6 that there is another type of large vanadium–vanadium interactions that is not considered in the literature, that is the V_1 – V_3 interaction. Indeed, the NN V_1 and V_3 magnetic orbitals are bridged by a p_y oxygen orbital that mediates the interactions between them. EHTB calculations confirm the present remarks with an evaluation of the transfer integral of $0.20 eV$ and $0.23 eV$. Of course this p_y oxygen orbital will mediate a super-exchange mechanism so that the magnetic interaction can be expected to be large and antiferromagnetic.

Summarizing the above results, one sees that the structure of the dominant interactions, both transfer and magnetic, does not follow the crystallographic zig-zag chains structure. Actually, the dominant interactions are arranged in two types of two-leg ladders, namely the V_2 – V_2 ladders and the V_1 – V_3 ladders which are crystallographically orthogonal to each other. The average filling of these ladders is of one electron for 3 sites in systems doped with divalent cations and of one electron for 6 sites in systems doped with monovalent cations. All magnetic interactions within these ladders show an antiferromagnetic character.

Let us now analyze the interactions between these ladders. The coupling between two V_1 – V_3 ladders could go either through V_1 – V_1 NN interactions which we have seen to be totally negligible, both in terms of electron transfer and magnetic interactions, or through the V_3 – V_3 NN interactions. The latter are somewhat larger than the NN V_1 – V_1 interactions but still quite weak and ferromagnetic in character.

Are there other types of inter-ladder interactions? Going back to figure 3, one sees that the V_1 , V_2 and V_3 pyramids share a corner.

Let us note the local axes in the following manner : y for the b direction, x and z in such a way that the V_1 and V_3 magnetic orbitals are d_{xy} and the V_2 magnetic orbitals are d_{zy} in nature.

The p_y orbitals of the V_1 – V_2 – V_3 bridging oxygen mediates the V_1 – V_3 interaction. One should notice that despite the nearly 90° V_1 – O – V_2 and V_3 – O – V_2 angles, the oxygen p_y orbital can efficiently mediate the transfer interaction between i) the V_1 and V_2 magnetic orbitals and ii) the V_3 and V_2 magnetic orbitals. This is due to the fact that, unlike the classical case, the V_n magnetic orbitals are orthogonal to the (V_1, O, V_2) and (V_3, O, V_2) planes. Indeed, EHTB calculations yield V_1 – V_2 and V_3 – V_2 transfer integrals of the order of $70 meV$ and $25 meV$. As far as the magnetic exchange is concerned, the p_y orbital is able to mediate super-exchange mechanism. Thus the effective exchange between the V_1 – V_3 and V_2 – V_2 ladders i) goes through the local V_1 – V_2 and V_3 – V_2 interactions, ii) can be expected to be weak but much larger than the exchange between two V_1 – V_3 ladders and iii) is antiferromagnetic in character.

In conclusion one can see the β - AV_6O_{15} compounds as composed of two types of orthogonal two-legs ladders packed in an 'IPN' geometry (see figure 7) and coupled

through antiferromagnetic exchange interactions.

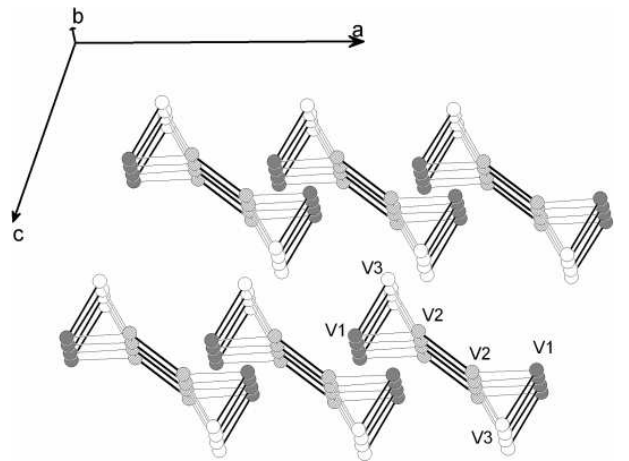


FIG. 7: Structure of the dominant interactions in the β - AV_6O_{15} compounds. Strong intra-ladder interactions are in dark gray, while inter-ladder interaction are pictured in light gray.

III. ON SITE ENERGIES

In the β - AV_6O_{15} compounds, the ladder rungs are built on two crystallographically different vanadium atoms. This is obviously the case for the V_1 – V_3 ladders and often for the V_2 – V_2 ladders. For instance, even in the high temperature phase, the Sr and Ca compounds present a dimerization along the b direction so that the V_2 – V_2 ladder rungs are composed of V_{2a} and V_{2b} crystallographically different atoms. These crystallographic differences, which are system and phase specific, are due to different chemical parameters such as the size of the A^{n+} cation, its location (in the β or β' sites), or the electronic instabilities toward spin-Peierls type of distortion. The consequence of these characteristics is that the energies of the two vanadium magnetic orbitals in one ladder rung are different. EHTB calculations show that these energy differences are not negligible, even in the high temperature phases, since they can reach values as large as $0.18 eV$ on the V_2 – V_2 ladders. Surprisingly the V_1 – V_3 ladders are much more symmetric with an orbital energy difference between the V_1 and V_3 magnetic orbitals of $0.05 eV$ only.

The first consequence is that there should be a charge/spin order, even in the high temperature phases. The second one is that the average fillings, η_{13} and η_{22} , of the two types of ladders have no reason to be equal and that a charge transfer degree of freedom between the two ladders should be taken into account.

IV. THE LOW TEMPERATURE PHASE

Similar EHTB calculations as those detailed in the preceding sections were done on the low temperature phase (LTPh). Structural data at 90K were taken from reference¹⁴. In the low temperature phase the unit cell is tripled along the ladder axis b . Sellier *et al* attributed this $3 \times b$ super-cell to small displacements of the V_2 atoms within the V_2 ladders rungs.

As expected, the results in the LTPh exhibit on-site orbital energies and transfer integral modulations compared to the high temperature phase (HTPh), however the main conclusions remain unchanged. Indeed, as in the HTPh, the dominant interactions are arranged in antiferromagnetic ladders, and these ladders are then antiferromagnetically coupled according to an IPN geometry. The main difference between the two phases is that while in the HTPh the transfer between IPNs is always very small, in the LTPh some of the V_3 - V_3 transfers are of the same order of magnitude as the intra-IPN ones. Another point to be noticed is that the variation range of the on-site orbital energies along the ladders is larger in the LTPh than in the HTPh. These differences can thus be expected to induce a greater electron localization in the ladder direction (in agreement with the observed metal to insulator transition) and a somewhat lesser 1D character in the LTPh.

V. DISCUSSION AND CONCLUSION

One of the troubling properties of the β - AV_6O_{15} compounds is that, while their crystallographic structure is very different from that of the α' - NaV_2O_5 system, they present very similar features, both in the optical conductivity and Raman spectra. The present study partially explains these similarities. Indeed, the electronic structures of the two compounds are based on similar units, despite their a-priori different crystallographic structures. They show (i) square-pyramid environment of the vanadium atoms with magnetic orbitals orthogonal to a very short vanadyl bond, and (ii) dominant interactions of the magnetic centers arranged in two-leg ladders with antiferromagnetic interactions.

The vanadyl multiple bond is responsible for the existence of a sharp peak around 1000 cm^{-1} in the Raman spectra of both β and α compounds. Other features related to the existence of the pyramidal entities are present in the Raman spectra of both type of compounds such as the bending mode between two pyramids around 440 cm^{-1} . Finally, one retrieves in both compounds the broad feature in the 550 cm^{-1} to 700 cm^{-1} range that was attributed in the α' - NaV_2O_5 to the electron-phonon coupling¹⁹ responsible for the spin-Peierls transition.

The optical conductivity spectra for both the β - AV_6O_{15} and the α' - NaV_2O_5 compounds also present strong similitudes, such as the famous 1 eV peak. This peak was attributed in the α' - NaV_2O_5 system to the first

doublet-doublet excitation energy on the ladder rung. It is also present in the β -type compounds, which are ladder systems, as well. In the SrV_6O_{15} , this peak is double (0.85 eV and 1.2 eV ¹²). In the assumption that this peak can also be attributed to the first doublet-doublet excitation energy of the ladder rungs, the doubling would be in total agreement with the electronic structure proposed in this work, namely two-leg ladders of two different types.

The occurrence of this peak in the β -type compounds raises several more general questions on 1D vanadium oxides.

- The first one is whether the existence of this 1 eV feature is the signature of a ladder arrangement of the dominant interactions in the vanadium oxides.
- It has been shown in the α' - NaV_2O_5 compound that the ladder rung should not be seen as supporting one electron delocalized on the two vanadium magnetic orbitals, but rather three magnetic electrons, since the bridging oxygen shows a strong open-shell character and the local wave-function is multiconfigurational^{7,15}. The second question is thus whether this magnetic character of the rung bridging oxygen is a general feature of the vanadium oxides with a two-leg ladders electronic structure.
- The third question is whether the 1 eV peak is the signature of this magnetic character of the rung oxygens. One of us is actually running ab-initio calculations in order to check these questions in the β compounds. The preliminary results confirm these hypotheses.

Finally let us remember that the sodium phase of the β - AV_6O_{15} family presents a super-conducting phase. Put into perspective with the present results yielding a ladder structure for the dominant interactions, one can wonder whether this compound could be a realization of the predicted superconductivity in doped ladder systems²⁰.

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Appendix

V ₁ -V ₃ ladder					
Rungs			Legs		
Atoms	t	$\Delta\varepsilon$	Atoms	t	$\Delta\varepsilon$
V _{1b} -V _{3b}	-0.203	0.050	V _{1a} -V _{1b}	-0.173	0.00
V _{1a} -V _{3a}	-0.237	0.113	V _{1a} -V _{1b+b}	-0.145	0.00
			V _{3a} -V _{3b}	-0.148	-0.038
			V _{3a} -V _{3b+b}	-0.140	-0.040

V ₂ -V ₂ ladder					
Rungs			Legs		
Atoms	t	$\Delta\varepsilon$	Atoms	t	$\Delta\varepsilon$
V _{2a} -V _{2b}	-0.313	-0.184	V _{2a} -V _{2b}	-0.147	-0.173
			V _{2a} -V _{2b+b}	-0.135	0.215

Inter-ladder Intra-IPN					
Rungs			Legs		
Atoms	t	$\Delta\varepsilon$	Atoms	t	$\Delta\varepsilon$
V _{2a} -V _{1a}	0.070	0.135	V _{2a} -V _{3a}	-0.024	-0.022
V _{2b} -V _{1b}	0.094	-0.046	V _{2b} -V _{3b}	0.054	0.093

Inter-ladder Inter-IPN					
Rungs			Legs		
Atoms	t	$\Delta\varepsilon$	Atoms	t	$\Delta\varepsilon$
V _{3a} -V _{3a'}	0.023	0.002	V _{3a} -V _{3b'}	-0.053	-0.038
V _{3b} -V _{3b'}	-0.059	0.006	V _{3b} -V _{3a-b}	-0.053	-0.038

TABLE I: EHTB values of the hopping and vanadium magnetic orbital energies (eV).

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