Electronic and magnetic structure of CsV$_2$O$_5$

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I. INTRODUCTION

Low-dimensional spin-gapped quantum systems are of current interest since they show interesting ground states and a variety of unconventional low-lying excitations. Examples of such systems include spin-1 Haldane chains, spin-$\frac{1}{2}$ even-leg ladders, and spin-$\frac{1}{2}$ alternating chains. The discovery of appropriate compounds like Y$_2$BaNiO$_4$ (Haldane chain), Sr$_4$Cu$_2$O$_{11}$ or SrCu$_2$O$_2$ (ladder systems) has brought new insight into the study of these systems. There is a long list of various spin-$\frac{1}{2}$ alternating chain systems which are being intensively studied in connection to their magnetic excitations, to mention a few of them KCuCl$_2$, TiCuCl$_4$, Cu(NO$_3$)$_2$.$_2$.D$_2$O. If frustration is also present new features appear in the magnetization spectrum of the low-dimensional quantum systems, as in CuGeO$_3$, (VO)$_2$P$_2$O$_7$ (VOPO)$_3$ and Cu$_2$(BO$_3$)$_2$. or in the recently synthesized Cu$_5$Te$_2$O$_9$Br$_2$.

An important family of low-dimensional compounds are the layered vanadates AV$_2$O$_5$ (A=Ca, Mg, Na, Li, Cs). While CaV$_2$O$_5$ and MgV$_2$O$_5$ contain only magnetic V$^{4+}$ ions and behave like spin-$\frac{1}{2}$ ladders with spin-gaps of the order of 600K and 20K respectively, $\alpha'$-NaV$_2$O$_5$, $\gamma$-LiV$_2$O$_5$ and CsV$_2$O$_5$ are mix-valence systems (V$^{4.5+}$ on average) with important charge and spin fluctuations. This last property makes this family specially interesting since it allows to study the influence of charge-ordering and the corresponding crystallographic distortions on the magnetic interactions. The quarter-filled ladder compound $\alpha'$-NaV$_2$O$_5$ is a highly discussed material and has become a model substance for the study of spin, charge and orbital coupling. It behaves like a spin-$\frac{1}{2}$ Heisenberg system at high temperatures and at 34K undergoes a charge ordering ($2V^{4.5+} \rightarrow V^{4+} + V^{5+}$) transition accompanied with a lattice distortion and the opening of a spin gap. $\gamma$-LiV$_2$O$_5$ is a charge ordered system with no spin gap opening at low temperatures. Recent investigations based on an $ab$ initio analysis of the electronic structure show that charge fluctuations in this system are still significant and the experimental observation can be well described by a spin-$\frac{1}{2}$ asymmetric quarter-filled ladder model. Such proposal has also found support by a numerical analysis of optical conductivity experiments. The third member of this vanadate family, CsV$_2$O$_5$, has been given much less attention. Existing susceptibility measurements of Isobe et al. could be rather well explained by considering this material as a system of isolated dimers with a spin-gap of $\approx 12$ meV. Measurements other than that are unknown to us except for older susceptibility measurements which somewhat disagree with Isobe et al.'s data and different values of the exchange integral $J$ and the gyromagnetic ratio $g$ are predicted.

There are various reasons why we believe that this system deserves attention: (i) the question of how the electronic and magnetic properties of this material compare with the properties of the other two members of the alkali-vanadate family, i.e. $\alpha'$-NaV$_2$O$_5$ and $\gamma$-LiV$_2$O$_5$ (ii) this system crystallizes in a similar monoclinic structure as the most discussed VOPO and many other materials e.g. KCuCl$_3$, TiCuCl$_3$ showing an alternating chain behavior of the magnetic interactions. It is then worthwhile to find out whether CsV$_2$O$_5$ has also a similar behavior of the magnetic interactions as its isostructural members. (iii) as will be shown below, a re-examination of the susceptibility measurements reveals that a dimer model is not the only model that can provide reasonable fitting of the susceptibility data.

In view of the above, we have performed a microscopic study of this system by considering Density-Functional-Theory-based (DFT) calculations. The microscopic study of the electronic behavior of this compound reveals that the inter-dimer coupling in this material in addition to the intra-dimer interaction is also significant and shouldn't be neglected. Further, an analysis of the susceptibility data shows that getting estimates of the coupling constants and the gyromagnetic factor based merely on a fitting procedure is very subtle and with such an analysis one can only test the consistency with the assumed model, but cannot prove the uniqueness of that model. Results on that will be presented in the next sections. We shall also discuss the similarities...
and differences to the other members of this vanadate family, \( \alpha' \)-NaV\(_2\)O\(_5\) and \( \gamma \)-LiV\(_2\)O\(_5\) as well as to isostructural compounds like VOPO.

II. CRYSTAL STRUCTURE

The crystal structure of CsV\(_2\)O\(_5\) is somewhat different from that of \( \alpha' \)-NaV\(_2\)O\(_5\) and \( \gamma \)-LiV\(_2\)O\(_5\). \( \alpha' \)-NaV\(_2\)O\(_5\) and \( \gamma \)-LiV\(_2\)O\(_5\) crystallize in the orthorhombic space group \( \text{Pmnn} (D\text{\textsubscript{2h}}\text{\textsuperscript{4}}) \) and \( \text{Pnma} (D\text{\textsubscript{2h}}\text{\textsuperscript{5}}) \) respectively. They consist of a double chain-structure of edge-sharing distorted square VO\(_5\) pyramids running along the orthorhombic \( y \) axis, which are linked together via common corners to form layers. These layers are stacked upon each other along \( z \). Na/Li atoms are located between these layers. CsV\(_2\)O\(_5\) crystallizes in the monoclinic space group \( P2_1/c \text{\textsubscript{5}} (C\text{\textsubscript{2h}}\text{\textsuperscript{5}}) \). CsV\(_2\)O\(_5\) has also a layered structure with Cs ions in between the layers. These layers, which are somewhat tilted (i.e., not strictly in \( yz \) plane), and are stacked upon each other along \( x \), are made of two types of vanadium atoms V1 and V2. The V1 atoms are in a distorted square pyramidal environment of oxygens and form pairs by sharing the edge of the pyramids. These pairs are separated from one another by the V2 vanadiums in a tetrahedral co-ordination of oxygens as shown in Fig. 1. Within a pair of square pyramids, the two apical O atoms are pointing in opposite directions and the remaining O atoms of the pyramids are shared with tetrahedra. The V1-V1 distance across the shared edge of the square-pyramids-pair is 3.073 Å and the V1-V2 distance across the shared corner of a pyramid and a tetrahedron is 3.352 Å. Since the average V2-O distance within the tetrahedron \( d=1.718 \) Å is shorter than the average V1-O distance within the square pyramid \( d=1.882 \) Å, one can conclude from a bond-valence analysis that the V1 sites are in the oxidation \( V^{4+} \) and the V2 sites are in the oxidation \( V^{5+} \). As the intra-pair \( V^{4+}\text{-}V^{4+} \) distance is 3.073 Å while the inter-pair distance along the \( z \)-axis is 5.501 Å, this compound has been assumed to be a system of isolated dimers.

III. BAND STRUCTURE

In order to analyze the electronic behavior of CsV\(_2\)O\(_5\), we carried out DFT calculations within the Local Density Approximation (LDA) by employing the full-potential linearized augmented plane wave code WIEN97 [28] and by linear-muffin-tin orbital (LMT) [29] based on the Stuttgart TBLMTO-47 code. Both calculations agree well within the allowed errorbars of the various different approximations involved in two different methods. In both approaches we treated the exchange-correlation part by using the generalized gradient approximation [30].

In Fig. 2 the energy bands for CsV\(_2\)O\(_5\) along the path \( \Gamma B D Z Y I Y E \) are shown. Since the unit cell of CsV\(_2\)O\(_5\) contains four formula units, i.e. four \( V^{4+} \) and four \( V^{5+} \), there are four bands around the Fermi level which correspond to \( V^{4+}\text{-}3d \) orbitals. These bands are separated by an energy gap of about 2 eV from the lower O-p valence bands and an energy gap of about 0.5 eV from the upper conduction bands. The conduction bands up to 4 eV are of \( V\)-3d nature. There are a few points to be noted here: (i) The energy range on the CsV\(_2\)O\(_5\) bands is of the same order of magnitude as it is in \( \alpha' \)-NaV\(_2\)O\(_5\) and \( \gamma \)-LiV\(_2\)O\(_5\). (ii) The contribution of \( V^{5+}\text{-}3d \) is mostly in the upper conduction bands, starting from about 0.75 eV above the Fermi level and have a very small contribution at the Fermi level indicating that, contrary to \( \alpha' \)-NaV\(_2\)O\(_5\) and \( \gamma \)-LiV\(_2\)O\(_5\), the system is close to complete charge ordering. (iii) There is no dispersion along the \( x \) axis while along the \( z \) axis (chain direction) the dispersion is non-negligible and of about 300meV. Along the \( y \) axis the LDA-bands show a small dispersion which corresponds to inter-chain interactions. In order to investigate the dimension-dependent behavior of CsV\(_2\)O\(_5\), we show in Fig. 3(a) the partial density of states (DOS) of the \( V^{4+} \) 3d-orbitals for CsV\(_2\)O\(_5\). For comparison we have also plotted in Fig. 3(b) the partial density of states of \( V\)-3d orbitals for \( \gamma \)-LiV\(_2\)O\(_5\) and in Fig. 3(c) that of V-3d orbitals for \( \alpha' \)-NaV\(_2\)O\(_5\). Note that, while the \( \gamma \)-LiV\(_2\)O\(_5\) and \( \alpha' \)-NaV\(_2\)O\(_5\) DOS show the characteristic quasi-1D van Hove singularities near the band edges around the Fermi level, this is not the case for the Cs-compound. The DOS for CsV\(_2\)O\(_5\) shows a 2D-behavior than 1D. (iv) In the global frame of reference, the character of the bands around the Fermi level turn out to be that of \( d_{xz}\) with small admixture from \( d_{z^2}\) character. Rotation to local coordinate system with the \( z \)-axis aligned along the \( \langle V\text{-apical } O \rangle \) direction for individual pyramids transform this to \( d_{xy} \) character, in agreement with the crystal-field analysis of a \( V^{4+} \) ion in the pyramidal environment.

The band-structure analysis leads us to the conclusion that inter-dimer coupling is non-negligible. If the system would have been a pure dimer system we would have expected no dispersion in any direction. The existence of a non-negligible dispersion tells us that a model of unlinked dimers is too simple and there must be some inter-dimer coupling to explain the band picture. From the DOS analysis we learn that inter-dimer interactions in both \( z \) and \( y \) direction are important for the electronic properties. The possible role of the \( V^{5+}\text{-}O_4 \) tetrahedra in this context will be investigated in the next section.

IV. MICROSCOPIC MODEL (EFFECTIVE MODEL)

In order to understand the nature of the ground state in CsV\(_2\)O\(_5\) we need to determine the appropriate microscopic model which explains the low-energy physics
of this compound. We have therefore applied the so-called downfolding method offered by the new and generalized version of the LMTO method, together with a tight-binding (TB) analysis on the band-structure results. The downfolding technique consists of integrating out the high energy degrees of freedom so as to describe the details of LDA energy bands close to the Fermi energy in terms of few-orbital effective Hamiltonians. From this analysis, we can extract the effective hopping matrix elements $t_{ij}$ between vanadium ions in CsV$_2$O$_5$ (by Fourier Transform of the downfolded Hamiltonian $H(k) \rightarrow H(R)$) which reproduce the behavior of the LDA bands close to the Fermi level is very small, and the biggest contribution doesn’t account for the band-splittings in the paths $\Gamma - n$, $s$ the path in between two edge-sharing square pyramids, $t_1$ in $\alpha'$-NaV$_2$O$_5$ and $\gamma$-LiV$_2$O$_5$ corresponds to a $V - O - V$ path between two corner-sharing square pyramids. This feature has important implications in the strength of the exchange interaction as has been pointed out in Ref. 4. Also note that the same kind of edge-sharing pyramids are also present in $\alpha'$-NaV$_2$O$_5$ and $\gamma$-LiV$_2$O$_5$ with effective hopping values smaller than $t_0$ and similar to $t_1$ in CsV$_2$O$_5$.

About the nature of the rest of the hopping integrals in CsV$_2$O$_5$, we observe that $t_2$, $t_3$ and $t_5$ correspond to $V^{4+}$-$V^{4+}$ paths through the bridging $V^{5+}$O tetrahedra with different lengths and angles. Beltran et al. studied, based on geometrical considerations, the various super-exchange paths for the case of vanadyl phosphates. In particular they considered the VOPO compound. VOPO and CsV$_2$O$_5$ have a similar monoclinic structure if one identifies the $P^{5+}$O tetrahedra and the $V^{4+}$O$_5$ square pyramids in VOPO with the $V^{5+}$O$_4$ tetrahedra and the $V^{4+}$O$_5$ square pyramids in CsV$_2$O$_5$ respectively. As argued by Beltran et al., based on the formation of coherently molecular electron orbitals, the coupling between two $V^{4+}$ through bridging oxygens for separated pyramids is weaker than those via the pathways involving $V^{5+}$ ions. Furthermore, double bridging modes, involving two $V^{5+}$ ions, as in $t_2$ and $t_3$ (see Fig. 3) can be stronger than single bridging modes involving one $V^{5+}$ ion as in $t_5$. These interactions can be as strong as paths of the type $t_1$, i.e. $V^{4+}$-O-$V^{4+}$ where the square pyramids are linked to each other by sharing an edge. Geometry considerations then lead to a relative order of importance among the various bridging modes, which for CsV$_2$O$_5$ is observed to be $t_3 > t_5 > t_2$. We note here that while in CsV$_2$O$_5$ we have seen that the dimers are formed by the edge-sharing pyramids ($t_1$) with the predominant inter-dimer interaction formed by $V^{4+}$-$V^{4+}$ interaction bridged by $V^{5+}$O$_4$ ($t_3$), in VOPO these roles are interchanged in the sense that dimers are formed by $V^{4+}$O$_5$ square pyramids bridged by $P^{5+}$O$_4$ groups ($t_3$) and the inter-dimer interaction is formed by neighboring $V^{4+}$O$_5$ pyramids ($t_1$). This is due to the different type of distortion in the square pyramids as well as different angle and distance relations between these two compounds.

Using the relation $J_1 = 4t_1^2/U$, $U$ being the on-site Coulomb electron-electron interaction and considering $U \sim 2.8$ eV, the DFT calculation gives an estimate of the intra-dimer exchange coupling, $J_1 \sim 225K$.

To summarize, the conclusions that we draw from the above analysis is that ab initio calculations support an alternating chain behavior for CsV$_2$O$_5$ along $z$ with weaker inter-chain interactions along $y$. 

\[ H_{TB} = - \sum_{i < j} t_{ij} (c_i^+ c_j + c_j^+ c_i) \]  

(1) 

where $i$ and $j$ denote a pair of $V^{4+}$ ions labeled each one by $(n, s)$ where $n$ denotes the unit cell and $s = 1, 2, 3, 4$ $V^{4+}$ ions in the unit cell. In Fig. 3 all the considered hoppings $t_1$, $t_2$, $t_3$ and $t_5$ have been drawn. The subscript 1, 2, 3 and 5 indicate respectively that the hopping integral is between first nearest neighbors (n.n.), second n.n., third n.n. and fifth n.n. The hopping term $t_4$, which connects two $V^{4+}$ ions belonging to two different layers along $x$, has been neglected due to its vanishingly small value. Note here that no hopping terms have been considered along the $x$ direction, since as we have learnt from the band picture, there is no dispersion along this direction and that means that the interlayer coupling along $x$ must be negligible. In Fig. 3 we show a comparison of the downfolding-TB bands to the LDA bands. We observe that not only the hopping corresponding to the intra-dimer interaction $t_1$ is important but also the inter-dimer matrix element $t_3$ along $z$ is considerable. A model with only $t_1$ and $t_3$, i.e. alternating chain, shows a dispersion relation of the form:

\[ E = \pm \sqrt{t_1^2 + t_3^2 + 2t_1t_3\cos k_z} \]  

(2) 

which is symmetric with respect to $E = 0$ (i.e. to $E_F$) and doesn’t account for the band-splittings in the paths $\Gamma - D$ and $\Gamma - Y$. These features are described by the interchain hopping parameters along the $y$ direction, $t_2$ and $t_5$, though they are much smaller than $t_1$ and $t_3$. Note that the TB-results show an artificial band-crossing along the path $B - D$ and $Z - \Gamma$. We have analyzed this result and seen that the inclusion of longer-ranged interactions lifts this artificial crossing.

Concerning the nature of the hopping integrals, we observe that the values of the dominant hopping parameter $t_1 = 0.12eV$ (which agrees with the overall band-width of the $V^{4+}$-$d_{xy}$ derived low-energy bands in CsV$_2$O$_5$) is smaller than the dominant hopping parameter for $\alpha'$-NaV$_2$O$_5$, $t_0 = 0.37eV$ and $\gamma$-LiV$_2$O$_5$, $t_0 = 0.35eV$. This difference can be explained by the nature of the path. While $t_1$ in CsV$_2$O$_5$ corresponds to a $V - O - V$ path in between two edge-sharing square pyramids, $t_1$ in $\alpha'$-NaV$_2$O$_5$ and $\gamma$-LiV$_2$O$_5$ corresponds to a $V - O - V$ path between two corner-sharing square pyramids. This feature has important implications in the strength of the exchange interaction as has been pointed out in Ref. 4. Also note that the same kind of edge-sharing pyramids are also present in $\alpha'$-NaV$_2$O$_5$ and $\gamma$-LiV$_2$O$_5$ with effective hopping values smaller than $t_0$ and similar to $t_1$ in CsV$_2$O$_5$.
In order to test the results obtained from the \textit{ab initio} calculation we only have available two sets of susceptibility data. As a function of temperature which don’t completely agree quantitatively with each other. We consider here the data by Isobe \textit{et al.}. These authors proposed that their experimental data are well fitted by the susceptibility of a spin-$\frac{1}{2}$ dimer system with \( H = JS_1S_2 \) given by:

\[
\chi_{\text{raw}} = \chi_{\text{CsV}_2O_5} + \chi_{\text{imp}}
\]

\[
= \frac{Ng^2\mu_B^2}{k_BT} \frac{1}{3 + \exp(J/k_BT)} + \chi_0 + \chi_{\text{imp}}
\]

with a g-factor of 1.8, \( J = 146K \) and \( \chi_0 = 8 \times 10^{-5} \text{emu/mol} \). We have re-analyzed the data by considering the temperature dependence of the susceptibility for a spin-$\frac{1}{2}$ alternating Heisenberg chain with:

\[
H = \sum_n (J_1S_{2n} \cdot S_{2n+1} + J_2S_{2n+1} \cdot S_{2n+2}).
\]

with \( J_1 > 0 \) and \( J_2 > 0 \) (antiferromagnetic couplings) obtained by the stochastic Quantum Monte Carlo method. We define the parameter \( \alpha = J_2/J_1 \) which measures the ratio of the inter and intra-dimer coupling. \( \alpha = 0 \) corresponds to the dimer model. We introduce also an additional parameter \( \delta \) so that \( J_1 = J(1 + \delta) \), \( J_2 = J(1 - \delta) \) and therefore \( \alpha = \frac{1 - \delta}{1 + \delta} \).

In Fig. 3(a) we show the comparison of the experimental data to the dimer-model susceptibility given by Eq. 3. We find, in fact, that the best fit corresponds to \( J = 146K \), \( \chi_0 = 8 \times 10^{-5} \text{emu/mol} \) and a value of \( g = 1.77 \), somewhat smaller than the one proposed in Ref. 2. Figs. 3(b) and (c) show the comparison of the experimental data to the spin-$\frac{1}{2}$ alternating Heisenberg chain model for \( \delta = 0.8, \alpha = 0.11 \) and \( \delta = 0.6, \alpha = 0.25 \) respectively. We observe that values of \( \alpha \) up to 0.25 give still very good fits to the susceptibility data by choosing appropriate \( g \) and \( J \) parameters. This analysis makes plausible our \textit{ab initio} results, namely the fact that the inter-dimer interactions can be also significant.

The important conclusion that we gain from this susceptibility analysis is that it is a very hard task to determine the behavior of a compound only from susceptibility fits. Extra information is needed so as to minimize the possible options. For instance, electron spin-resonance (ESR) experiments could complement the susceptibility measurements by delivering the value of the gyromagnetic factor. There are in the literature other examples (\textit{e.g.} VOPO) where the only examination of the susceptibility led to a wrong interpretation of the behavior of the system.

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FIG. 1. Crystal structure of CsV$_2$O$_5$ projected in the (yz) plane (see text for explanation). The large circles are the V-ions, black and grey for V$^{4+}$ and V$^{5+}$ respectively. The oxygens are represented by the smaller circles. Pairs of edge-shared distorted V$^{4+}$O$_5$ square pyramids are bridged by V$^{5+}$O$_4$ tetrahedra to form layers. The alkali-ion Cs shown by white circles, are located in between these sheets.

FIG. 2. DFT results for CsV$_2$O$_5$. The path is along $\Gamma=(0,0,0), B=(-\pi,0,0), D=(-\pi,0,\pi), Z=(0,0,\pi), \Gamma, Y=(0,\pi,0), E=(-\pi,\pi,\pi)$. Also shown in rectangles is the band character (in the local coordinate system) where $V1=V^{4+}$ and $V2=V^{5+}$. 

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FIG. 3. Partial density of states of the V$^{4+}$-3d orbitals in (a) CsV$_2$O$_5$, (b) γ-LiV$_2$O$_5$, (c) α′-NaV$_2$O$_5$ obtained from DFT. Compare the distinct behavior at band edges around the Fermi level.

FIG. 4. Hopping parameters corresponding to the tight-binding modeling of CsV$_2$O$_5$. Not shown is the on-site energy $\varepsilon_0$ of the V$^{4+}$ site. While $t_1$ corresponds to a direct V$^{4+}$-O-V$^{4+}$ superexchange path, $t_2$, $t_3$ and $t_5$ are defined by pathes through the neighboring V$^{5+}$O$_4$ tetrahedra.

FIG. 5. Comparison of the tight-binding bands (solid lines) with the DFT bands (dashed lines). The tight-binding parameters (see Fig. 4) are (in eV) $\varepsilon_0 = -0.0215$, $t_1 = 0.117$, $t_2 = 0.015$, $t_3 = 0.097$, $t_5 = 0.050$. 
FIG. 6. Temperature dependence of the magnetic susceptibility of CsV$_2$O$_5$. The dots correspond to the experimental data by Isobe et al. where the Curie contribution has been subtracted. The solid lines show a fit to (a) spin-$\frac{1}{2}$ Heisenberg dimer with $J/k_B$=146 K, $g$ = 1.77, (b) spin-$\frac{1}{2}$ alternating Heisenberg chain with $\delta$ = 0.8, $J_1/k_B$=146 K, $g$ = 1.79 and (c) spin-$\frac{1}{2}$ alternating Heisenberg chain with $\delta$ = 0.6, $J_1/k_B$=146 K, $g$ = 1.81.