Ab initio evaluation of the charge-ordering in $\alpha'NaV_2O_5$

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We report ab initio calculations of the charge ordering in $\alpha'NaV_2O_5$ using large configurations interaction methods on embedded fragments. Our major result is that the 2$p_x$ electrons of the bridging oxygen of the rungs present a very strong magnetic character and should thus be explicitly considered in any relevant effective model. The most striking consequence of this result is that the spin and charge ordering differ substantially, as differ the experimental results depending on whether they are sensitive to the spin or charge density.

The problem of charge ordering in the $\alpha'NaV_2O_5$ compound has been widely discussed since Isobe et al. discovered in 1996 that this compound presents a spin-Peierls transition at 34K. From the first X-ray structural determination by Carpy and Galy a charge ordering was assumed in the compound. Indeed, the $P2_1mn$ non-centrosymmetric group yielding two inequivalent vanadium atoms, it supported the hypothesis of an electronic structure formed by an alternation of magnetic $V^{4+}$ chains and non-magnetic $V^{5+}$ chains. When a spin-Peierls transition was found it interpreted through the dimerization of the magnetic chains seemed quite obvious. In 1998, the reinvestigation of the high temperature (HT) crystal structure yielded a $Pmmn$ centrosymmetric group for which the equivalence of all vanadium atoms lifted any grounding to the charge ordering. The controversy was raised again by Damascelli et al. in 1998. The strong on-rung doublet-doublet absorption band, observed in the optical conductivity spectrum around $\Delta E = 1eV$, was attributed by the authors to a charge transfer excitation of the magnetic electron between the two vanadium atoms. This picture assumes a strong charge order on the rung (of about 0.8 electron), however both the crystallographic data and the $^{51}V$ NMR studies exhibit only one type of vanadium atom.

It is now widely accepted that the $\alpha'NaV_2O_5$ spin-Peierls transition is in fact a double transition, consisting in a magneto-distortion of the lattice following a charge ordering of the unpaired electrons. X-ray and electron diffraction experiments led to propose for the low temperature (LT) phase a $Fmm2$ symmetry group associated with a doubling of the unit cell in the $a$ and $b$ directions while it is quadrupled in the $c$ direction. This low temperature symmetry yields two inequivalent, but very similar, $V_2O_5$ layers, each of them containing three inequivalent vanadium atoms. $^{51}V$ NMR experiments see however only two inequivalent sets of vanadium atoms. In order to explain these experimental results, a large number of hypotheses have been proposed for the electronic structure of the low temperature phase. Among these hypotheses the partisans of a total charge ordering ($V^{5+}$ and $V^{4+}$ sites) are the most numerous. They suppose either the same alternation of magnetic $V^{4+}$ and diamagnetic $V^{5+}$ chains that was first suggested for the high temperature phase, or a zig-zag charge ordering along the ladders. More in agreement with the X-ray structural symmetries, but not with the NMR results, is the hypothesis of two alternated ladders, one supporting two equivalent $V^{4.5+}$ atoms and the other a zig-zag $V^{5-}V^{4+}$ charge ordering. Fewer authors suggest that the charge ordering is only partial and that one should consider the previous charge localizations hypotheses with a $V^{4.5\pm\delta}$, $\delta < 0.5$ charge ordering.

The aim of the present ab-initio quantum chemical calculations is to investigate the local electronic structure of the compound in order to better understand — and solve some of the controversies of — the charge ordering both in high and low temperature phases. For this purpose we used a method of ab-initio spectroscopy of embedded crystal fragments, using large atomic basis sets and large differential configurations interactions methods dedicated to the accurate evaluation of both transitions energies and states wave-functions for a detailed description of the method applied to this system see our paper on the evaluation of $t - J$ and two-band Hubbard models for the high temperature phase. This method has been successfully used both in molecular magnetic systems and in strongly correlated materials in order to determine super-exchange or hopping integrals with an exceptional accuracy. The bath is designed in order to model the major effects (Madelung and Pauli exclusion) of the rest of the crystal on the fragment, that is in such a way that the crystal density of states projected on the atomic orbitals (the most crucial being the magnetic and bridging orbitals) is accurately reproduced in the embedded fragment. This goal is reached through a combination of punctual charges and total-ions pseudo-potentials (TIP) for more details and validity checks on the
The magnetic sites are not the vanadium atoms by themselves but the whole $V-O-V$ rungs (as first suggested by Horsch [16]),

- these magnetic sites do not support one delocalized or partly delocalized magnetic $3d$ electron but that the $2p$ electrons of the bridging oxygen atoms — supported by the $2p_y$ orbital pointing along the $b$ axis — present also a strong magnetic character.

Indeed the computed wave-functions (reported below for the HT and LT fundamental doublets) for the fundamental, as well as first excited, doublet states exhibit a strong contribution on the configurations where the $2p_y$ orbital of the bridging oxygen is half-filled. In fact the magnetic problem on the rungs should not be considered as one magnetic electron delocalized between the $3d_{xy}$ of the two vanadium atoms but rather as a resonance between this configuration ($\alpha|d_p\bar{p}\rangle + \beta|p\bar{p}d_j\rangle$ where $d_i$ and $d_j$ respectively stand for the magnetic $3d_{xy}$ orbitals of the two vanadium atoms and $p$ for the $2p_y$ orbital of the bridging oxygen atom) and the configuration with three magnetic electrons respectively localized on the magnetic $3d_{xy}$ orbitals of two vanadiums and the $2p_y$ orbital of the bridging oxygen ($- (\gamma + \delta) |d_i\bar{p}d_j\rangle + \gamma|\bar{d}_ipd_j\rangle + \delta|d_ip\bar{d}_j\rangle$).

The wave function of the HT fundamental doublet of the rungs is

\[ +0.63 \left( |d_p\bar{p}\rangle + |p\bar{p}d_j\rangle \right)/\sqrt{2} \]
\[ +0.68 \left( -2|d_i\bar{p}d_j\rangle + |\bar{d}_ipd_j\rangle + |d_i\bar{p}d_j\rangle \right)/\sqrt{6} \]
\[ +0.13 \left( |\bar{d}_id_j\rangle + |d_id_j\rangle \right)/\sqrt{2} \]
\[ +0.12 \left( |d_ip\rangle - |pd_j\rangle \right)/\sqrt{2} \]
+ small terms . . .

The LT phase is known [1] for presenting an alternation (along the $\bar{a}$ direction) between modulated and non-modulated ladders as well as two slightly different $(a,b)$ planes. While one out of two ladders remains of similar geometry as in the high temperature phase, the other ladder takes a small zig-zag form along the $b$ direction. The results on the non-modulated rungs are very similar as in the HT phase and will not be further detailed. The wave functions of the LT fundamental doublets on the modulated rungs are

\[ +0.25(0.23)|d_p\bar{p}\rangle + 0.59(0.60)|p\bar{p}d_j\rangle \]
\[ +0.53(0.52)|d_i\bar{p}d_j\rangle - 0.40(0.41)|\bar{d}_ipd_j\rangle - 0.13(0.11)|d_i\bar{p}d_j\rangle \]
\[ +0.11(0.11)|\bar{d}_id_j\rangle + 0.06(0.06)|d_id_j\rangle \]
\[ -0.06(0.05)|d_i\bar{p}d_j\rangle + 0.09(0.09)|pd_j\rangle \]
+ small terms . . .

where the number in parentheses correspond to the alternate $(a,b)$ plane.

The first consequence of the strong magnetic character of the bridging oxygen atom is that it should be explicitly considered while modeling the compound. One of the most striking implication is that while in the single magnetic electron picture the charge and spin sites populations are equal when 3 magnetic electrons are considered the charge and spin sites populations can strongly differ. Table 1 displays the charge and spin population of the magnetic orbitals.

|          | Charge populations | Spin populations |
|----------|--------------------|------------------|
|          | $d_i$   | $d_j$ | $d_i$ | $d_j$ | $d_i$ | $d_j$ |
| HT phase | 0.785   | 1.43  | 0.785 | 0.58  | -0.16 | 0.58  |
| LT non Mod. | 0.78    | 1.44  | 0.78  | 0.575 | -0.15 | 0.575 |
| LT Mod.  | 0.61    | 1.45  | 0.94  | 0.22  | -0.10 | 0.88  |

*TABLE 1. Magnetic orbitals charge and spin populations on the rungs (in electrons units). Note that on the modulated rungs the $V_i-O$ distance is shorter than the $V_j-O$ distance.*
One should notice that while the 3d charge population ordering on the modulated rungs is only $\delta_{ch} = 0.33$, the participation of the oxygen to magnetic properties results in a spin population ordering nearly twice as large with $2\delta_{sp} = 0.66$. On the non-modulated rungs however, as expected from the crystallographic data, there is not any charge ordering and the overall results are very similar to the high temperature phase. One should however notice that the charge and spin populations remain substantially different, with a strong increase of the 3d population (compared to the 0.5 value expected in the one magnetic electron picture) and a smaller increase of the spin polarization of the 3d orbitals by inverse polarization on the central oxygen 2p orbital.

Another result worth to be pointed at is the substantial differences we found between the magnetic orbitals charge populations and the total atomic populations. It is well known that such total population calculations are partly dependent to the choice in the atomic basis set, and in particular to the spatial extension of the latter. It is however widely accepted in quantum chemistry that the population variations are significant and reliable evaluations of charge transfer processes. Table II therefore presents the computed atomic populations variations through the transition.

| V$_i$ | V$_j$ | O | V$_i$ | V$_j$ |
|------|------|---|------|------|
| Charge | -0.005 | +0.000 | -0.005 | +0.007 | -0.001 | -0.038 |
| Spin | -0.002 | +0.005 | -0.002 | -0.37 | +0.05 | +0.32 |

**TABLE II.** Variation of the total atomic charge and spin populations (in number of electrons units) in the low temperature phase with respect with the high temperature phase. Note that on the modulated rungs the $V_i$–O distance is shorter than the $V_j$–O distance.

One notices immediately that while the atomic total spin population results are totally coherent with the magnetic orbital spin populations reported in table I, the atomic total charge populations are substantially different from the magnetic orbital charge populations. Indeed while the total charge disproportion between the two vanadium atoms of the modulated rungs is extremely small ($2\delta_{chtot} = 0.045$), the disproportion between the two 3d magnetic orbital populations is $2\delta_{ch} = 0.33$.

A finer analysis of the electrons repartition in term of atomic orbitals shows that there are substantial electron population transfers between the vanadium magnetic 3d$_{xy}$ orbitals and the other 3d vanadium orbitals.

Indeed, while the V$_j$ atom sees its total number of electron decrease, the occupation of its 3d$_{xy}$ atomic magnetic orbital increases by 0.143 electron due to a population transfer from the 3d$_{x^2-y^2}$, 3d$_{z^2}$ and 3d$_{xz}$ orbitals. On the V$_i$ atom the population transfer goes in reverse order and the atomic magnetic orbital looses 0.166 electron in favor of the 3d$_{x^2-y^2}$, 3d$_{z^2}$ and 3d$_{xz}$ orbitals (see table III, IV).

| d$_{xy}$ | d$_{x^2-y^2}$ | d$_{z^2}$ | d$_z$ |
|---------|--------------|-----------|-------|
| 0.309   | -0.136       | -0.088    | -0.085 |

**TABLE III.** Orbital population difference between the V$_j$ and V$_i$ atoms of the modulated rungs in the low temperature phase. Units are in number of electron.

| Atom | d$_{xy}$ | d$_{x^2-y^2}$ | d$_{z^2}$ | d$_z$ |
|------|---------|--------------|-----------|-------|
| V$_i$ | -0.166  | +0.068       | +0.044    | +0.047 |
| V$_j$ | +0.143  | -0.068       | -0.044    | -0.038 |

**TABLE IV.** Difference between the 3d orbitals populations of the two vanadiums of the rungs in the LT phase (modulated rungs) and the HT phase.
This electron transfer can be understood if one considers that the 2p$_x$ doubly-occupied orbital of the bridging O atoms strongly overlaps with the 3d$_{x^2-y^2}$, 3d$_z$ and 3d$_{xz}$ orbitals of the vanadiums. $V_1$ being closer to the oxygen than $V_2$ by 0.13 Å, the larger overlap between the oxygen 2p$_x$ and the vanadium 3d$_{x^2-y^2}$, 3d$_z$ and 3d$_{xz}$ orbitals increases the occupation of the latter orbitals. The opposite phenomenon acts on the $V_2$ atom. Such an increase in the 3d atomic population would result in a proportional increase of the on-site repulsion unless another valence orbital, close to the Fermi level, is simultaneously de-populated. This is precisely the case with the magnetic 3d$_{xy}$ orbital. The combined result of this $d \rightarrow d$ transfers and the magnetic character of the bridging oxygen results in a strong difference between the total charge ($2\delta_{\text{chtot}} = 0.05$) and the spin ($2\delta_{\text{aplot}} = 0.69$) orderings.

The consequence of this analysis, and this is one of the major conclusions of the present work to draw this unexpected result, is that experiments sensitive to the local charge density and experiments sensitive to the local spin density should yield substantially different results.

Summarizing our results on the charge ordering, we have found (in agreement with the crystallographic data) that there is neither charge nor spin ordering in the high temperature phase, that there is neither charge nor spin ordering on the non-modulated rungs in the low temperature phase and that while the total charge ordering is very small on the modulated rungs, the spin ordering is on the contrary quite large.

In the HT phase, our results agree nicely both with the $^{51}$V NMR studies (as them we see only one type of vanadium atom) and optical conductivity measurements. Indeed, our computed on-rung doublet-doublet excitation energy is 1.08eV which compares very well with the 1eV optical conductivity peak.

In the LT phase Presura et al. conclude from optical conductivity experiments, that there should not be any major charge redistribution through the phase transition, in full agreement with our results. The apparent contradiction between these results and the inelastic neutron scattering experiments that predict large charge ordering can also be lifted. Indeed, the latter are sensitive to the spin ordering which we have seen to be very different from the charge ordering, due to the magnetic nature of the bridging oxygen of the rung. Finally, the $^{51}$V NMR experiments predict only two different types of vanadium atoms in the LT phase. NMR experiments are sensitive to the electronic spin polarization at the vanadium nuclei, that is essentially the spin polarization of the vanadium $s$ orbitals induced by the spin polarization of the magnetic sites. A simple energetic perturbative argument shows that the major contribution to this spin polarization must be supported by the vanadium $4s$ orbitals. Indeed, the $4s$ orbitals are the only ones close enough to the Fermi level to interact with the magnetic electrons in a non negligible way. We therefore computed the induced spin polarization on the vanadiums $4s$ orbitals. On modulated rungs we found a spin $4s$ population of 0.244 × 10^{-2} on $V_1$ and 1.51 × 10^{-2} on $V_2$ while on the non-modulated rungs we found 0.005 × 10^{-2}, that is two order of magnitude lower. As a title of comparison the spin vanadium $4s$ polarization is in the HT phase 0.9 × 10^{-2}. It seems therefore possible to explain the NMR experiments in the low temperature phase by the fact that the induced spin polarization on the $s$ orbital of the non-modulated rungs vanadium atoms is so low that their signal is not observed in the experimental window.

The main message we would like to send as a conclusion is that the $\alpha'$NaV$_2$O$_5$ compound should not so much be considered as a quarter-filled system with one magnetic electron delocalized on the two vanadiums of each ladder rung, but rather as a resonating system where the $V - O - V$ rungs support three magnetic electrons on the magnetic orbitals, namely the $d_{x^2}$, $d_{y^2}$ of the vanadium atoms and the $p_x$ orbital of the bridging oxygen. A major consequence of this result is that, on the LT-modulated rungs, the charge and spin ordering are different. Indeed, while the charge ordering is very small, the spin ordering is quite large. The direct implication is that experiments sensitive to the spin density and experiments sensitive to the charge density should not yield similar ordering amplitudes. We therefore think that a reinterpretation of experimental measurements in view of the present results could solve most of their apparent inconsistencies.

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