Exchange interactions and magnetic properties of the layered vanadates CaV$_2$O$_5$, MgV$_2$O$_5$, CaV$_3$O$_7$ and CaV$_4$O$_9$

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We have performed ab-initio calculations of exchange couplings in the layered vanadates CaV$_2$O$_5$, MgV$_2$O$_5$, CaV$_3$O$_7$ and CaV$_4$O$_9$. The uniform susceptibility of the Heisenberg model with these exchange couplings is then calculated by quantum Monte Carlo method; it agrees well with the experimental measurements. Based on our results we naturally explain the unusual magnetic properties of these materials, especially the huge difference in spin gap between CaV$_2$O$_5$ and MgV$_2$O$_5$, the unusual long range order in CaV$_3$O$_7$ and the "plaquette resonating valence bond (RVB)" spin gap in CaV$_4$O$_9$.

The series of insulating vanadates with the composition MV$_n$O$_{2n+1}$ is of considerable interest because it shows a variety of strange magnetic phenomena which are not completely understood. Among these quasi-two dimensional layered materials CaV$_2$O$_5$ has originally attracted a lot of attention as the first two-dimensional material with a gap in the spin excitation spectrum [1], but for MgV$_2$O$_5$ the magnetic exchange coupling for 180$^\circ$ ferromagnetic one for 90$^\circ$ bonds, the interactions in these vanadates are much more complicated. Not even the sign of exchange interactions can give information about relative and absolute values of the exchange couplings in these systems.

In this Letter we report on such an ab-initio calculation using the LDA+U method [13] to compute the electronic structure and from it the exchange couplings. We then use the quantum Monte Carlo (QMC) method to calculate the uniform susceptibility assuming these exchange couplings, and compare it with experimental measurements. We find good agreement and are thus confident that our explanation of the magnetic properties of these materials captures the relevant physics.

The LDA+U method was shown to give good results for insulating transition metal oxides with a partially filled d-shell [14]. The exchange interaction parameters can be calculated using a procedure based on the Greens function method which was developed by A.I. Lichtenstein [3]. This method was successfully applied to calculate the exchange couplings in KCuF$_3$ [10] and in layered cuprates [17].

The LDA+U method [3,[4] is essentially the Local Density Approximation (LDA) modified by a potential correction restoring a proper description of the Coulomb interaction between localized d-electrons of transition metal ions. This is written in the form of a projection operator:

$$\hat{H} = \hat{H}_{LSDA} + \sum_{mm'} |inlm\sigma)V_{mm'}^{\sigma}(inlm'\sigma| \ (1)$$

$$V_{mm'}^{\sigma} = \sum_{\{m\}} \{U_{m,m',m''}n^{\sigma}_{m''} + (U_{m,m',m''}) - U(N - \frac{1}{2}) + J(N^\sigma - \frac{1}{2})$$

where $|inlm\sigma)$ (i denotes the site, n the main quantum number, l orbital quantum number, $m$ magnetic number and $\sigma$ spin index) are d-orbitals of transition metal ions. The density matrix is defined by:

$$n_{mm'}^{\sigma} = -\frac{1}{\pi} \int_{E_F} G_{inlm, inlm'}^{\sigma}(E)dE, \ (2)$$

where $G_{inlm, inlm'}^{\sigma}(E)$ are the elements of the Green function matrix, $N^\sigma = Tr(n^{\sigma}_{mm'})$ and $N = N^\uparrow + N^\downarrow$. $U$ and $J$ are screened Coulomb and exchange parameters. The $U_{mm',m''}^{\sigma}$ is the screened Coulomb interaction among the nl electrons which can be expressed via integrals over complex spherical harmonics and $U$ and $J$ parameters. For the CaV$_2$O$_{2n+1}$ compounds the values of these parameters were calculated to be $U=3.6$ eV, $J=0.88$ eV via the so-called "supercell" procedure [15]. The calculation scheme was realized in the framework of the Linear Muffin-Tin

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Orbitals (LMTO) method [19] based on the Stuttgart TBLMTO-47 computer code.

The inter-site exchange couplings were calculated with a formula which was derived using the Green function method as second derivative of the ground state energy with respect to the magnetic moment rotation angle [13, 14]:

$$J_{ij} = \sum_{\{m\}} I_{m'm''}^{ij} \chi_{mm'm''}^{ij}$$

(3)

where the spin-dependent potentials $I$ are expressed in terms of the potentials of Eq. [10],

$$I_{m'm''}^{ij} = V_{m'm''}^{ij} - V_{mm''}^{ij}.$$  

(4)

The effective inter-sublattice susceptibilities are defined in terms of the LDA+U eigenfunctions $\psi$ as

$$\chi_{mm'm''}^{ij} = \sum_{kmn} \frac{n_{nk} \psi_{lkm}}{\epsilon_{nk}} \psi_{lmn}^{\star} \psi_{lmn}^{\prime} \psi_{lmn}^{\prime} \psi_{lmn}^{\prime \prime}.$$  

(5)

The main building block of the crystal structures of the Ca$\text{V}_n\text{O}_{2n+1}$ series is a V ion roughly in the center of a pyramid of oxygen ions. The lowest energy orbital is the V3d-orbital of $xy$-symmetry (using a convention where the axes of the coordinates system are directed toward the oxygen ions in the plane), which is the orbital whose lobes look at the directions where the overlap with the oxygen is the smallest. The crystal field splitting between $xy$-orbital and other 3d-orbitals is so strong, that in the LDA band structure the $xy$-band is separated from the rest of V3d-bands by a small energy gap [13].

As a consequence the degeneracy of the V3d-shell is lifted and the single $d$ electron of V$^{4+}$ ion occupies this $xy$-orbital, which reminds us of the cuprates, with a single hole in the $x^2-y^2$-orbital. The important difference is that while in cuprates all copper atoms are in the same $(x, y)$-plane as the $x^2-y^2$-orbital, in these vanadates the vertices of the pyramids point alternatingly up and down with respect to the basal plane. Thus the V ions in their centers are correspondingly above and below the central plane, as can be seen in Fig. 1. As the $xy$-orbitals are parallel to this plane, the overlap (and hence the exchange couplings) are expected be stronger for vanadium ions situated on the same side of the plane. We will show that this is indeed the case. In addition to this alternation, a tilting of the pyramids is present in the crystal structure of these compounds, which seriously influences the interactions.

Another important difference with the cuprates is that the $xy$-orbital has a $\pi$-overlap with the in-plane oxygen atoms in contrast to a much stronger $\sigma$-overlap in case of Cu$^{2+}$. Consequently one can expect much weaker exchange interaction in vanadates as compared to cuprates. All the more surprising is thus the fact that the spin gap in Ca$\text{V}_3\text{O}_5$ (616K [10]), is larger than the typical values for the similar cuprate ladders ($\approx 460$ K [20]).

Equation (3) was derived as a second derivative of the total energy with respect to the angle between spin directions of the LDA+U solution. The LDA+U method is the analogue of the Hartree-Fock (mean-field) approximation for a degenerate Hubbard model [14]. While in the multi-orbital case a mean-field approximation gives reasonably good estimates for the total energy, for the non-degenerate Hubbard model it is known to underestimate the triplet-singlet energy difference (and thus the value of the effective exchange coupling $J_{ij}$) by a factor of two for a two-site problem ($E_{HF} = \frac{2t^2}{U}$ and $E_{exact} = \frac{4t^2}{U}$, where $t \ll U$ is inter-site hopping parameter). In the problem under consideration there are two types of contributions to the exchange interaction parameters $J_{ij}$. The first one is due to the $xy - xy$ orbitals hopping, and as only this orbital is half-filled this contribution directly corresponds to the non-degenerate Hubbard model and its value must be multiplied by a factor of two to correct the Hartree-Fock value. Other contributions are due to the hoppings to all other orbitals and as the mean-field approximation is much better for multi-orbital model this part can be used unmodified.

| TABLE I. Calculated exchange coupling parameters (K). “Minus” sign means ferromagnetic exchange. |
| Ca$\text{V}_3\text{O}_5$ | Mg$\text{V}_2\text{O}_9$ | Ca$\text{V}_3\text{O}_7$ | Ca$\text{V}_4\text{O}_9$ |
|-----------------|-----------------|-----------------|-----------------|
| $J_1$            | $-28$           | $60$            | $46$            | $62$            |
| $J_2$            | $608$           | $92$            | $-14$           | $89$            |
| $J_3$            | $122$           | $144$           | $75$            | $148$           |
| $J_4$            | $20$            | $19$            | $18$            | $91$            |
| $J_5$            | $5$             |                |                |                |

In the crystal structure of these MV$_n$O$_{2n+1}$ compounds layers are formed by VO$_2$ pyramids sharing edges of their bases. The V atoms of the layer form roughly square lattice which is $1/(n+1)$-depleted (Fig. 2). As mentioned earlier, the strongest interaction must be between V atoms which are situated on the same side of the plane (above or below) and are marked by the light gray and the dark gray circles in Fig. 2.
In the MV$_2$O$_5$ crystal structure these atoms form ladders with interactions along the rung and the leg of the ladder denoted as $J_2$ and $J_3$ and interaction between ladders as $J_1$ (the notations are chosen to reflect the interatomic distances; the shortest one is between atoms on different sides of the plane). In CaV$_3$O$_7$ the atoms on the same side of the plane form zigzag chains with interaction inside this chain denoted as $J_3$ and interactions between chains as $J_1$ and $J_2$. For CaV$_4$O$_9$ such atoms form "metaplaquettes" (this term was proposed by W.Pickett [10] to distinguish them from the plaquettes formed by atoms with the shortest V-V distance). The interaction inside the metaplaquette is denoted by $J_3$, between metaplaquettes on the same side of the plane as $J_4$, and between metaplaquettes on the opposite sides of the plane by $J_1$ and $J_2$.

Our calculated values of the exchange couplings are presented in the Table I. It can immediately be seen that indeed the strongest interactions are between atoms on the same side of the plane (the ladder exchanges $J_2$, $J_3$ for CaV$_2$O$_5$ and MgV$_2$O$_5$, the zigzag exchange $J_3$ for CaV$_3$O$_7$ and the metaplaquette exchange $J_3$ for CaV$_4$O$_9$). However all other parameters are not negligible and for CaV$_4$O$_9$ the frustrating interactions between metaplaquettes are not less than 60% of the value of interaction inside the metaplaquette.

For a comparison of these exchange couplings to measurements on the materials and to discuss the magnetic properties we consider the temperature dependence of the uniform susceptibility $\chi(T)$. This quantity depends very sensitively on the exchange constants and can be both easily measured in experiments and calculated numerically for the Heisenberg model. To calculate the $\chi(T)$ we use the continuous time version of the quantum Monte Carlo (QMC) loop algorithm [21]. This algorithm uses no discretization of the imaginary time direction and the only source of systematic errors are thus finite size effects. The lattice sizes were chosen large enough so that these errors are much smaller than the statistical errors of the QMC simulations. All of these simulations, with the exception of the model for CaV$_3$O$_7$ suffer from the negative sign problem due to frustration effects. Improved estimators [22] can be used to lessen this sign problem, as was done in Ref. [23] for similar models. The frustration is especially strong in MgV$_2$O$_5$ and CaV$_4$O$_9$. In these two cases $\chi(T)$ could not be calculated to temperatures far below the susceptibility maximum. However $\chi(T)$ at intermediate temperatures is already very sensitive to the values of the exchange couplings and a comparison is thus possible.

The $g$-factors for V$^{4+}$ ($d^1, S=1/2$) compounds are observed to be in a narrow range about $g=1.96$ [24]. We use this value to compare (in Fig. 3) the calculated $\chi(T)$ to measurements done by Isobe and Ueda [23] over a wide temperature range. Taking note that the purity of the samples, and thus the normalization of the experimental data, is not known precisely and keeping in mind how sensitive is $\chi(T)$ dependence to the values of the exchange couplings we find reasonable agreement of the calculated $\chi(T)$ with the experiments.

The agreement is especially good in the case of
CaV$_2$O$_5$ where the exchange coupling $J_2$ on the rung of the ladder is dominant. Our LDA+U results thus confirm the weakly coupled dimer picture proposed for this compound in [1,2].

The magnitude of the exchange coupling however depends strongly on the tilting of the oxygen pyramid. The compound MgV$_2$O$_5$ has nearly the same crystal structure as CaV$_2$O$_5$, but as the Mg ion has a smaller ionic radius than Ca ion, the tilting of the oxygen pyramids in MgV$_2$O$_5$ is stronger. This causes the exchange coupling on the rung $J_2$ to be more than four times smaller and explains the huge difference in the uniform susceptibilities and spin gaps of these two compounds.

The exchange couplings in MgV$_2$O$_5$ are all of the same order, which positions this material in the strongly frustrated region of the trellis lattice phase diagram [25], precisely the region about which not much is known yet. Even the experimental evidence is ambiguous, with different claims about the existence or non-existence of a small spin gap reported in the literature [6]. More detailed experimental investigations are in progress, which will help to understand not only this compound but also the properties of the strongly frustrated trellis lattice Heisenberg model.

Of the compounds under consideration only CaV$_3$O$_7$ has no frustration, and at low temperatures our QMC simulations gave a magnetically ordered Néel state, with the magnetic structure coinciding with the one observed in experiments. This structure, with ferromagnetic order on the short 3-atom "rungs" and antiferromagnetic order along the infinite chains could not be easily explained previously. The most surprising result is that the exchange couplings $J_3$ and $J_1$ which were thought to be equivalent [1] are actually of opposite sign, most probably due to the tilting in the lattice structures (Fig. 1). These exchange couplings also naturally lead to the observed experimental order, and no recourse to quantum fluctuation effects, as proposed by Kontani et al. [4], is necessary. While there is qualitative agreement between the calculated and measured susceptibilities it is not as good as in the other compounds, due to closeness to a ferromagnetic state and large cancellation effects in the effective exchange couplings that increase the errors of the LDA+U exchange coupling estimates.

Of the four compounds CaV$_2$O$_9$ is the most studied one. We find that indeed the originally proposed plaquette-RVB state [2] is relevant, but with the larger meta-plaquettes ($J_3$) being dominant, as suggested by Pickett [16] and by Kodama et al. [17]. However, in contrast to the estimates of [1] we find that the coupling $J_4$, while smaller than $J_3$, is comparable to the other exchange couplings.

Our estimated exchange couplings can explain the order of magnitude of the spin gap of CaV$_3$O$_9$. With our values of J’s the unfrustrated $J_3$-$J_4$ model was shown to have a spin gap [3] of about 60K, which is further increased by frustration due to $J_1$ and $J_2$ [7]. While exact theoretical estimates for the spin gap in this strongly frustrated regime are not available, this estimate agrees with the measured spin gap of 107K, and the good agreement between the measured and predicted uniform susceptibilities is a further indication for the validity of our estimates.

Additional comparisons can be done by calculating the magnon dispersion of the model and comparing it to experiments, as was recently done by Mambrini and Mila [11]. According to their data, obtained on a small 16-site cluster our ratio $J_3/J_1$ might just be slightly too large to give the dispersion minimum at (0,0), but further calculations on larger clusters are necessary to clarify this point.

To summarize, using LDA+U calculations of the exchange couplings for a series of layered vanadate compounds we can explain the puzzling magnetic properties of these materials and find good agreement between the ab-initio predictions for the uniform susceptibility and experimental measurements. Such calculations are especially needed for systems such as the vanadates investigated here, where not only relative strength, but even the sign of the exchange interaction can not be estimated using simple geometrical arguments. Applied to a series of layered vanadates we can explain the difference in spin gap of CaV$_2$O$_5$ and MgV$_2$O$_5$, obtain a natural explanation of the unusual magnetic order in CaV$_3$O$_7$ and confirm the plaquette-RVB state of CaV$_4$O$_9$ with ab-initio calculations.

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