Exchange Interactions and Magnetic Properties of the Layered Vanadates CaV_2O_5, MgV_2O_5, CaV_3O_7, and CaV_4O_9

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We have performed *ab initio* calculations of exchange couplings in the layered vanadates CaV_2O_5, MgV_2O_5, CaV_3O_7, and CaV_4O_9. The uniform susceptibility of the Heisenberg model with these exchange couplings is then calculated by the 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_2O_5 and MgV_2O_5, the unusual long range order in CaV_3O_7, and the "plaquette resonating valence bond" spin gap in CaV_4O_9.

The series of insulating vanadates with the composition MV_nO_{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_4O_9 has originally attracted a lot of attention as the first two-dimensional material with a gap in the spin excitation spectrum [1] attributed to a plaquette resonating valence bond (RVB) state [2]. The other members of this family are also of interest. CaV_3O_7 shows long range Néel order with an unusual ordering [3] that could not be explained by simple models [4]. CaV_2O_5 has a large spin gap of about 600 K [5], but for MgV_2O_5, on the other hand, which has nearly the same lattice structure, there is only contradicting evidence for a possibly gapped state with a much smaller gap of only about 20 K [6]. Despite extensive theoretical work on these materials [2,4,7–12] their magnetic properties are not yet understood. In contrast to planar cuprates, where a hole in x^2-y^2 orbitals of Cu results in a strong antiferromagnetic exchange coupling for 180° bonds and a weak ferromagnetic one for 90° bonds, the interactions in these vanadates are much more complicated. Not even the sign of many of the exchange couplings is obvious in these materials.

In this Letter we report on an *ab initio* calculation using the LDA + U method [13] to compute the electronic structure and from it the exchange couplings. The calculated values of the exchange couplings allow us to naturally explain the unusual magnetic properties of these vanadates. Good agreement of quantum Monte Carlo (QMC) simulations of the uniform susceptibility assuming these exchange couplings with experimental measurements further supports the accuracy of the calculated exchange couplings.

The LDA + U method [13,14] 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. It was shown to give good results for insulating transition metal oxides with a partially filled d shell [14]. The intersite 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 [15,16]. This method was successfully applied to calculate the exchange couplings in $KCuF_3$ [16] and in layered cuprates [17].

For the vanadates discussed here the screened Coulomb and exchange parameters $U = 3.6$ eV, $J = 0.88$ eV were calculated via the "supercell" procedure [18]. The calculation scheme was realized in the framework of the linear muffin-tin orbitals (LMTO) method [19] based on the Stuttgart TBLMTO-47 computer code.

The main building blocks of the crystal structure are V atoms roughly in the center of a pyramid built of five oxygen atoms (see Fig. 1). These VO_5 pyramids share edges of their bases and form a layered structure of $1/(n + 1)$-depleted square lattice (Fig. 2). The lowest energy orbital is the V $3d$ 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 the xy orbital and other $3d$ orbitals is so strong that in the LDA band structure the xy band is separated from the rest of V $3d$ bands by a small energy gap [10]. As a consequence the degeneracy of the V $3d$ 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 plane, in these vanadates the vertices of the pyramids point alternately up and down with respect to the basal (x-y) plane. Thus the V ions in their centers are correspondingly above and below the central plane (marked as dark gray and light gray circles in Fig. 2), as can be seen in Fig. 1.
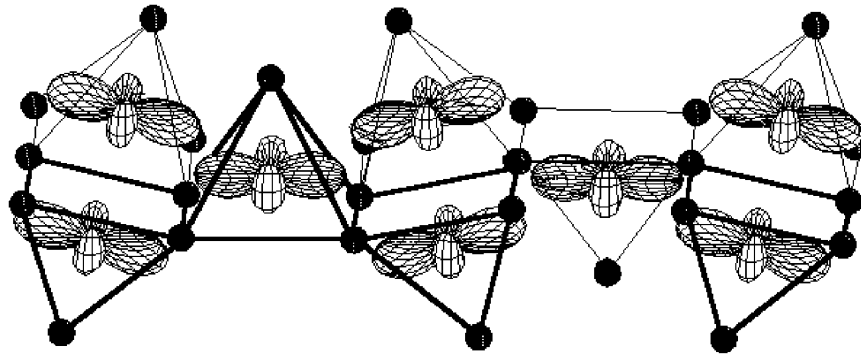
FIG. 1. The occupied d orbitals of V^{4+} ions in CaV_3O_7. Oxygen atoms (denoted as small solid circles) form pyramids with V atoms inside them.

Consequently, the exchange couplings are expected to be stronger for vanadium ions situated on the same side of the plane, which is confirmed by our calculations. 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 to the cuprates is that the xy orbital has a π overlap with the in-plane oxygen atoms in contrast to a much stronger σ overlap in the case of cuprates, leading us to expect much smaller exchange couplings. All the more surprising is the fact that the spin gap in CaV_2O_5 (616 K [5]), is *larger* than the typical values for the similar cuprate ladders (≈ 460 K [20]).

In the MV_2O_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_3O_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_4O_9 such atoms form "metaplaquettes" (this term was proposed by 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.

The LDA + U method is the analog of the Hartree-Fock (mean-field) approximation for a degenerate Hubbard model [14]. While in the multiorbital case a mean-field approximation gives reasonably good estimates for the total energy, for the nondegenerate 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 2 for a two-site problem ($E_{HF} = \frac{2t^2}{U}$ and $E_{exact} = \frac{4t^2}{U}$, where $t \ll U$ is intersite hopping parameter). In the problem under consideration there are two types of contributions to the exchange interaction parameters J_{ij}. One is due to the xy-xy orbitals hopping, and, as only this orbital is half-filled, this contribution directly corresponds to the nondegenerate Hubbard model and its value must be multiplied by a factor of 2 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 the multiorbital model, this part can be used unmodified.

Our calculated values of the exchange couplings are presented in Table I. It can immediately be seen that indeed the strongest interactions are between atoms on the same side of the plane. However, all other parameters are not negligible, and for CaV_4O_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 sensitively on the exchange constants and can be both easily measured in experiments and calculated for the Heisenberg
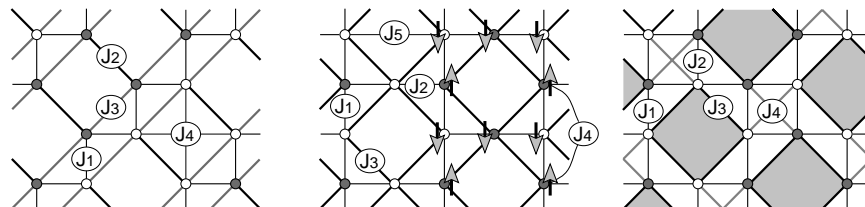

FIG. 2. The basic crystal structure and the notation of exchange couplings in CaV_2O_5 and MgV_2O_5 (left panel), CaV_3O_7 (middle panel), and CaV_4O_9 (right panel). V atoms represented by white and gray circles have different z coordinates. The long range magnetic structure of CaV_3O_7 is depicted by arrows. The metaplaquettes in the CaV_4O_9 structure are shaded in gray.

TABLE I. Calculated exchange couplings in units of kelvin. Negative couplings denote ferromagnetic exchange.

	CaV_2O_5	MgV_2O_5	CaV_3O_7	CaV_4O_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

model using the quantum Monte Carlo loop algorithm [21]. The only systematic errors in this algorithm are finite size effects, which we control by choosing large enough lattices [22].

All of these simulations suffer from the negative sign problem due to frustration effects. Improved estimators [23] can be used to lessen this sign problem. The frustration is especially strong in MgV_2O_5 and CaV_4O_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 sensitive to the values of the exchange couplings and a comparison is thus possible. We use a V^{4+} g factor of $g = 1.96$ [24] to compare (in Fig. 3) the calculated $\chi(T)$ to measurements done by Isobe and Ueda [25] 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 we find reasonably good agreement of the calculated $\chi(T)$ with the experiments. From the deviation of the temperatures where $\chi(T)$ is maximal we estimate a relative error of about 10% for the exchange couplings.

The agreement is especially good in the case of CaV_2O_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 [5,12]. The magnitude of the exchange coupling, however, depends strongly on the tilting of the oxygen pyramid. The compound MgV_2O_5 has nearly the same crystal structure as CaV_2O_5, but, as the Mg ion has a smaller ionic radius than the Ca ion, the tilting of the oxygen pyramids in MgV_2O_5 is stronger, causing the huge difference in the exchange couplings and spin gaps of these two compounds.

The exchange couplings in MgV_2O_5 are all of the same order, which positions this material in the strongly frustrated region of the trellis lattice phase diagram [26], precisely the region about which not much is known yet. Even the experimental evidence is ambiguous, with different claims about the existence or nonexistence of a small spin gap reported in the literature [6]. More detailed experimental investigations are in progress.

For CaV_3O_7 our QMC simulations gave a magnetically ordered Néel state at low temperatures, with the magnetic structure coinciding with the one observed in experiments. This structure, with ferromagnetic order on the short three-atom "rungs" and antiferromagnetic order along the infinite chains, could not be easily explained previously. The
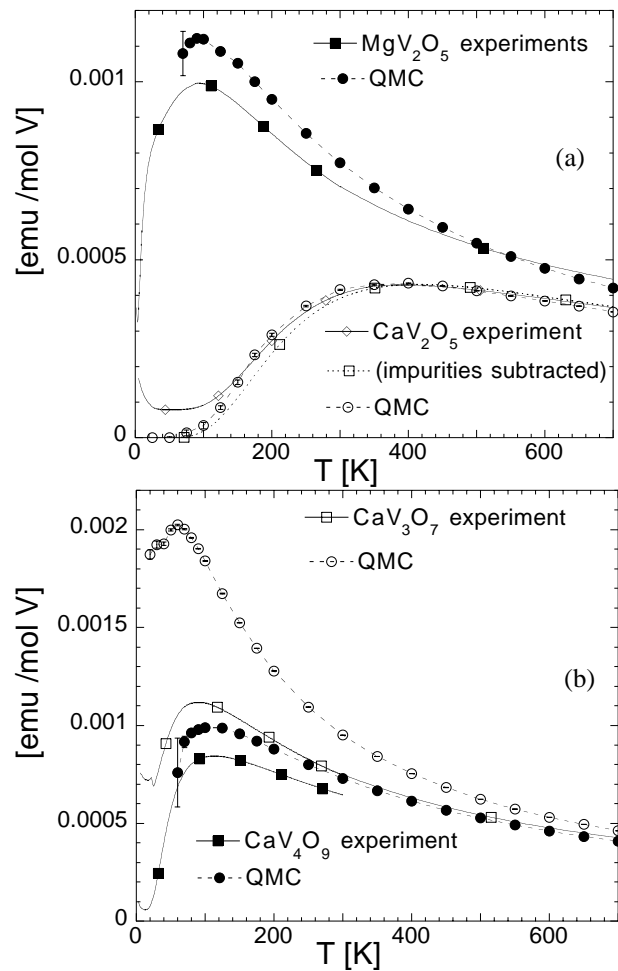

FIG. 3. Comparison of the temperature dependence of the uniform susceptibility $\chi(T)$ measured in experiments [25] to that calculated in QMC using the LDA + U values for the exchange coupling of (a) CaV_2O_5 and MgV_2O_5, (b) CaV_3O_7 and CaV_4O_9. The g factor of V^{+4} was taken to be $g = 1.96$ [24]. The agreement is very good, except for CaV_3O_7 where large cancellations in the effective exchange couplings increase the relative error.

most surprising result is that the exchange couplings J_2 and J_1 which were thought to be equivalent [4] 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 and long range magnetic orderings, it is not as good as in the other compounds, due to large cancellation effects in the effective exchange couplings that increase the relative errors of our estimates.

Of the four compounds CaV_4O_9 is the most studied. It was first proposed that the spin gap of this material originates in weakly coupled singlets on four spin plaquettes (connected by J_2) [2]. These four-spin singlets on the plaquettes were termed "plaquette-RVB" states. It was

later suggested [9,10] that the dominant coupling might be J_3, and that the larger metaplaquettes formed by the J_3 bonds are responsible for the spin gap. Our estimates for the couplings confirm this latter plaquette-RVB state, as J_3 is indeed the largest of the couplings. However, in contrast to the estimates of Kodama *et al.* [9] we find that the coupling J_4 is comparable to the other exchange couplings.

Our estimated exchange couplings can also explain the order of magnitude of the spin gap of CaV_4O_9. With our values of exchange couplings the unfrustrated J_3-J_4 model was shown to have a spin gap [2] of about 60 K, 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 107 K. The good agreement between the measured and calculated 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_4 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.

In summary, 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 cannot be estimated using simple geometrical arguments. Applied to a series of layered vanadates, we can explain the difference in spin gap of CaV_2O_5 and MgV_2O_5, obtain a natural explanation of the unusual magnetic order in CaV_3O_7, and confirm the plaquette-RVB state of CaV_4O_9 with *ab initio* calculations.

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