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Electronic structure and exchange interactions of the ladder vanadates CaV_2O_5 and MgV_2O_5

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Abstract. We have performed *ab initio* calculations of the electronic structure and exchange couplings in the layered vanadates CaV_2O_5 and MgV_2O_5 . On the basis of our results we provide a possible explanation of the unusual magnetic properties of these materials, in particular the large difference in spin gap between CaV_2O_5 and MgV_2O_5 .

1. Introduction

Spin-1/2 ladder models can describe the magnetic behaviour of a variety of quasi-one-dimensional systems [1]. Examples include the cuprate materials SrCu_2O_3 [2], $\text{LaCuO}_{2.5}$ [3], and $(\text{Sr}, \text{Ca})_{14}\text{Cu}_{24}\text{O}_{41}$ [4]. Spin excitations in the isolated ladders have a finite energy gap, which makes them prototype spin liquids. This is of interest in relation to high-temperature superconductivity, since upon doping they become resonating-valence-bond liquids, with a spin-excitation gap and dominant quasi-long-range pairing correlations [1].

Two more examples of the spin-1/2 ladder systems are the layered vanadate compounds CaV_2O_5 and MgV_2O_5 . Although CaV_2O_5 and MgV_2O_5 have nearly identical vanadium–oxygen planes, their magnetic properties are strikingly different. CaV_2O_5 has a large spin gap of about 600 K [5], while the spin gap in MgV_2O_5 is very small—only about 20 K [6]. In contrast to the case for the planar cuprates, where a hole in the Cu $x^2 - y^2$ orbitals results in a strong antiferromagnetic exchange coupling for the 180° bonds and a weak ferromagnetic one for the 90° bonds, the exchange interactions in these vanadates can be more complicated, as shown in figure 1. Even the signs of the many exchange couplings are not obvious for these materials. So one has to resort to *ab initio* numerical calculations to get information about the relative as well as the absolute values of the exchange couplings in these systems. The determination of the exchange couplings is crucial to the understanding of the markedly different spin-gap behaviour in these compounds.

In this paper, we shall report on the *ab initio* calculation of the exchange couplings using the LDA + U method and discover that they are indeed different in these two compounds, consistent with their magnetic properties. As the various exchange couplings are related to the bare hopping matrix elements, we shall extract them using a recently developed systematic downfolding scheme [7]. The advantage of the downfolding method is that only the important orbitals referred to as the active channels are retained in the basis and the rest are downfolded, thereby providing a single- or few-band tight-binding model capable of reproducing the details of the LDA bands close to a prescribed energy, which is usually the Fermi energy. We shall

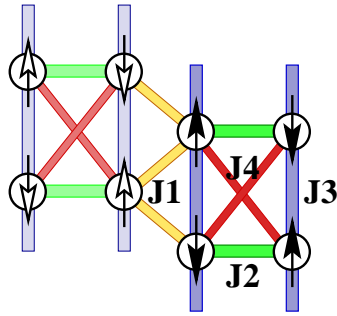


Figure 1. Various magnetic interactions in $\text{Ca}(\text{Mg})\text{V}_2\text{O}_5$ compounds. Two nearest vanadium ladders with different z -coordinates are shown in different shades. J_1 , the exchange interaction between nearest V atoms, is ferromagnetic for CaV_2O_5 and antiferromagnetic for MgV_2O_5 . J_2 and J_3 are respectively the antiferromagnetic exchange interactions along the rung and leg of the ladder. J_4 is the antiferromagnetic exchange interaction between the V atoms along the diagonal of the ladder. The magnetic structure used in the calculations is marked with up-pointing and down-pointing arrows. Half of the exchange interactions J_1 and all of exchange interactions J_4 are frustrated in this magnetic structure.

use such few-band models to extract the various hopping matrix elements. This will form a basis for understanding the widely different spin-gap behaviours in CaV_2O_5 and MgV_2O_5 .

The remainder of the paper is organized as follows. In section 2 we shall briefly recapitulate the crystal structure of CaV_2O_5 and MgV_2O_5 . In section 3 we shall present our LDA + U calculations for the various exchange couplings and compare them with available experimental results. Section 4 will be devoted to electronic structure calculations based on the TB-LMTO method [8], followed by the use of the downfolding method to extract the various hopping matrix elements, in order to explain the different exchange couplings in these materials. Finally, the conclusions are given in section 5.

2. Structure

The main building blocks of the crystal structures of $\text{Ca}(\text{Mg})\text{V}_2\text{O}_5$ compounds are the V ions, each roughly in the centre of a pyramid of oxygen ions, as can be seen in figure 2. The crystal structure of CaV_2O_5 is primitive orthorhombic with space group $Pm\bar{m}n$ and lattice constants $a = 11.35 \text{ \AA}$, $b = 3.60 \text{ \AA}$, and $c = 4.89 \text{ \AA}$. As shown in figure 2 (left), the structure is formed by a linkage of VO_5 pyramids having apex oxygens in the direction of the c -axis. Oxygen edge- and corner-shared zigzag V chains are formed along the b -axis, where the nearest-neighbour V–V distance is 3.03 \AA . Along the a -axis, these chains are linked by sharing corners with the V–V distance of 3.49 \AA . This forms a quasi-two-dimensional ladder layer in the ab -plane with the leg along the zigzag V chains (i.e. along b) while the rung is in the perpendicular direction (i.e. along a). The Ca atoms are located between the layers and are each surrounded by eight O atoms.

The crystal structure of MgV_2O_5 is base-centred orthorhombic with space group $Cmcm$; and lattice constants $a = 11.02 \text{ \AA}$, $b = 3.69 \text{ \AA}$, and $c = 9.97 \text{ \AA}$. Again, the structure can be described as a linkage of VO_5 pyramids having apex oxygens in the direction of the c -axis, as can be seen in figure 2 (right). The V zigzag chains extend along the a -axis by sharing edges and corners of the pyramids, and the nearest-neighbour V–V distance is 2.98 \AA . They are also

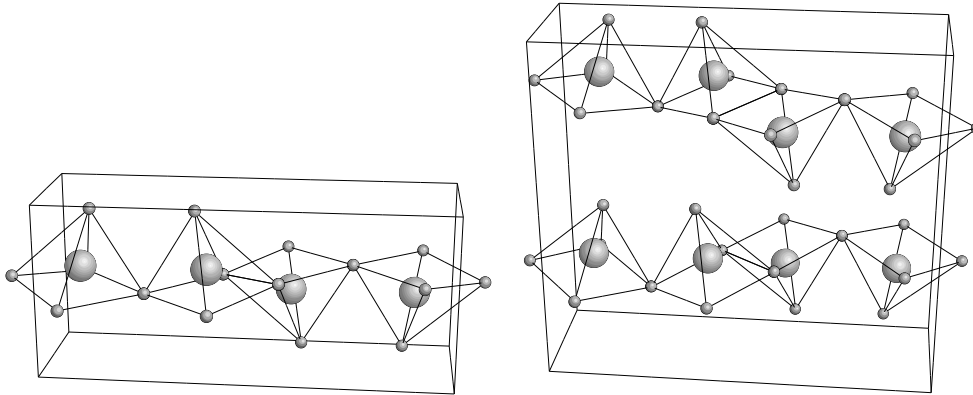


Figure 2. On the left the crystal structure of CaV_2O_5 and on the right the crystal structure of MgV_2O_5 . Ca and Mg atoms are not shown; large balls represent V atoms and small balls represent O atoms. In each figure the oxygen atoms constitute a pyramid; these pyramids are linked by edge and corner sharing as described in the text.

linked by sharing corners along the b -axis, with the V–V distance of 3.37 \AA , which again leads to quasi-two-dimensional ladder layers in the ab -plane. However, in contrast to the case for CaV_2O_5 , these layers stack alternately with the separation of $c/2$, and the Mg atoms are located between the layers and are each surrounded by six oxygen atoms. As a consequence, there is a puckering of the V_2O_5 layers to accommodate Mg ions in the tetrahedral coordination.

All the structural data that we have discussed above are summarized in table 1 and indicated in figure 3. It should be noted that as a consequence of the puckering of the V_2O_5 layers the tilting angle of the corner-sharing pyramids α (see figure 3) is appreciably smaller in MgV_2O_5 in comparison to CaV_2O_5 .

Table 1. Structural data for CaV_2O_5 and MgV_2O_5 compounds. The lattice constants (in \AA) are a along the rung of the ladder, b along the leg, and c in the vertical direction. The distances (in \AA) between nearest V ions between ladders, along the leg, along the rung, and along the diagonal are denoted as d_{nn} , d_{leg} , d_{rung} , and d_{diag} , respectively. The angle α (figure 3) is the V–O–V angle where the oxygen atom is placed between two vanadium atoms forming the rung. The angle β is the O–V–O angle where one oxygen is rung oxygen and the other is apical oxygen. Finally, the angle γ is the O–V–O angle with both the oxygen atoms in the leg direction. All angle values are listed in degrees.

Characteristic	CaV_2O_5	MgV_2O_5
a, b, c	11.35, 3.60, 4.89	11.02, 3.69, 9.97
$d_{nn}, d_{rung}, d_{leg} (=b), d_{diag}$	3.03, 3.49, 3.60, 5.02	2.98, 3.57, 3.69, 5.00
α, β, γ	132.91, 102.94, 135.29	117.57, 109.23, 141.15

3. The LDA + U and exchange couplings

The LDA + U method has been shown to give good results for insulating transition metal oxides with a partially filled d shell [9]. The exchange interaction parameters can be calculated using a procedure based on the Green-function method, developed by Lichtenstein *et al* [11, 12]. This method has been successfully applied to calculate the exchange couplings in KCuF_3 [12] and in layered cuprates [13].

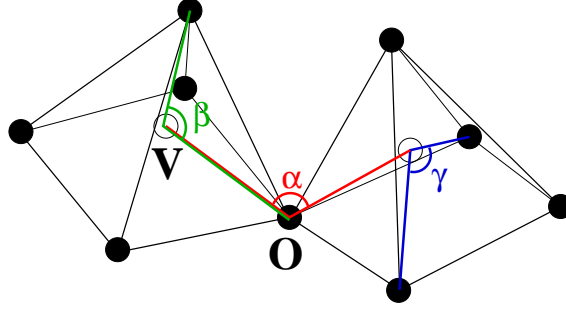


Figure 3. A pair of corner-sharing VO₅ pyramids. The various angles indicated in the figure are quoted in table 1.

The LDA + U method [9, 10] is the local density approximation (LDA) modified by a potential correction restoring a proper description of the Coulomb interaction between the localized d electrons of transition metal ions. This is written in the form of a projection operator:

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

where

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

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

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

where $G_{inlm,inlm'}^\sigma(E) = \langle inlm\sigma | (E - \hat{H})^{-1} | inlm'\sigma \rangle$ are the elements of the Green-function matrix, $N^\sigma = \text{Tr}(n_{mm'}^\sigma)$, and $N = N^\uparrow + N^\downarrow$. U and J are the screened Coulomb and exchange parameters. $U_{mm'm''m'''}$ is the screened Coulomb interaction among the nl -electrons, which can be expressed via integrals over complex spherical harmonics and the parameters U , J . For the Ca(Mg)V₂O₅ compounds the values of these parameters were calculated to be $U = 3.6$ eV and $J = 0.88$ eV via the so-called ‘supercell’ procedure [14] (in the ‘supercell’ calculation only the xy -orbitals were considered to be localized so that all other d orbitals could contribute to the screening). The calculation scheme was realized in the framework of the linear muffin-tin orbital (LMTO) method [15] based on the Stuttgart TBLMTO-47 computer code.

On the basis of the Green-function method, the inter-site exchange couplings can be derived as the second derivatives of the ground-state energy with respect to the magnetic moment rotation angle [11, 12]:

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

where the spin-dependent potentials I are expressed in terms of the potentials of equation (1):

$$I_{mm'}^i = V_{mm'}^{i\uparrow} - V_{mm'}^{i\downarrow}.$$

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

$$\chi_{mm'm''m'''}^{ij} = \sum_{knn'} \frac{n_{nk\uparrow} - n_{nk\downarrow}}{\epsilon_{nk\uparrow} - \epsilon_{nk\downarrow}} \psi_{nk\uparrow}^{ilm^*} \psi_{nk\uparrow}^{jlm''} \psi_{n'k\downarrow}^{ilm'} \psi_{n'k\downarrow}^{jlm''*}.$$

The LDA + U method is the analogue of the Hartree–Fock (mean-field) approximation for a degenerate Hubbard model [9]. 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 ($E_{HF} = 2t^2/U$ and $E_{exact} = 4t^2/U$, where $t \ll U$ is the inter-site hopping parameter).

As we discussed in section 2 the main building blocks of the crystal structures of the $\text{Ca}(\text{Mg})\text{V}_2\text{O}_5$ compounds are the V ions, each roughly at the centre of a pyramid of oxygen ions. The relevant point group symmetry is C_{4v} . The five d orbitals of the vanadium ion transform according to the following irreducible representations: $3z^2 - r^2$ (A_1), $x^2 - y^2$ (B_1), xy (B_2), and (xz, yz) (E). The lowest-energy orbital is the V 3d orbital of xy -symmetry (using a convention where the axes of the coordinate system are directed towards the oxygen ions), which is the orbital whose lobes point in the directions where the overlap with the oxygen is the smallest, as can be seen in figure 4.

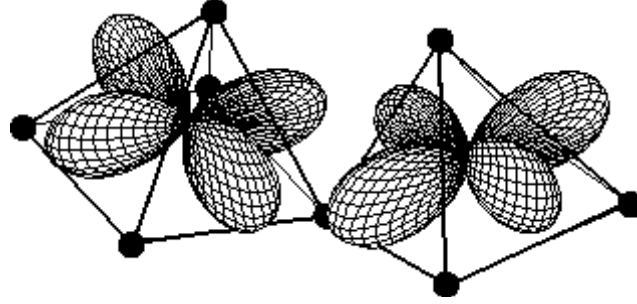


Figure 4. The angular distribution of the V d-electron spin density for two V atoms belonging to the rung. Oxygen pyramids enclosing the V atoms are also shown in the figure.

Due to the crystal-field splitting, the degeneracy of the V 3d shell is lifted and the single d electron of the 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 up and down alternately with respect to the basal plane. Thus the V ions at their centres are correspondingly above and below the central plane, as can be seen in figure 2. As the xy -orbitals are parallel to this plane, the overlaps (and hence the exchange couplings) are expected to be stronger for vanadium ions situated on the same side of the ladder 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 we shall see seriously influences the interactions.

Another important difference from 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 Cu^{2+} . Consequently, one can expect much weaker exchange interaction in vanadates as compared to

cuprates. However, it is surprising that the spin gap in CaV_2O_5 (616 K [5]) is *larger* than the typical values for the similar cuprate ladders (≈ 460 K [2]).

So in the problem under consideration there are two types of contribution to the exchange interaction parameters J_{ij} . The first one is due to the $xy - xy$ orbital 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 the multi-orbital model this part can be used without modification.

As mentioned earlier, the strongest interaction must be between V atoms which are situated on the same side of the plane (above or below) (see figure 1). These atoms form ladders with interactions along the rung and the leg of the ladder denoted as J_2 and J_3 respectively and the interaction between the ladders denoted as J_1 (the notation is chosen to reflect the inter-atomic distances; the shortest one is between the atoms on different sides of the plane).

Our calculated values of the exchange couplings are presented in table 2. It can be immediately seen that the strongest interactions are indeed between atoms on the same side of the plane (the ladder exchanges J_2, J_3). There is very strong anisotropy between the exchange interactions along the rung ($J_2 = 608$ K) and the leg ($J_3 = 122$ K) for CaV_2O_5 . However, for MgV_2O_5 the rung ($J_2 = 92$ K) and the leg ($J_3 = 144$ K) exchange interaction parameters are comparable in size.

Table 2. Calculated exchange coupling parameters (in K). The minus sign indicates ferromagnetic exchange.

	CaV_2O_5	MgV_2O_5
J_1	-28	60
J_2	608	92
J_3	122	144
J_4	20	19

Our results suggest that CaV_2O_5 is a system of dimers weakly coupled along the rung of the ladder with a very strong interaction inside the dimer. The analysis [16] based on fitting the results of model calculations to the experimental susceptibility measurements for CaV_2O_5 confirms the coupled-dimer picture, and one of the sets of parameters obtained ($J_2 = 665$ K, $J_3 = 135$ K, $J_1 = -25$ K) is very close to our *ab initio*-calculated parameter values. However, for MgV_2O_5 our calculations suggest $J_2/J_1 = 1.53$ and $J_3/J_1 = 2.40$ which puts MgV_2O_5 outside the scope of the ladder limit, consistent with the helical ordered gapless phase according to the phase diagram obtained by the Schwinger-boson mean-field theory [17]. Recently [18] the exchange parameters for CaV_2O_5 and MgV_2O_5 obtained in the LDA + U method were used for calculations of the uniform susceptibility of the Heisenberg model by the quantum Monte Carlo method. The results agree very well with the experimental measurements, and particularly good agreement has been found for CaV_2O_5 .

4. LDA band structures and hopping integrals

In this section, we shall investigate the origin of the strong anisotropy of the rung and leg exchange interactions in CaV_2O_5 and its absence in MgV_2O_5 using LDA band-structure calculations. We shall use a systematic downfolding scheme to obtain an effective single-band (or few-band) model Hamiltonian capable of reproducing the details of the LDA bands close to the Fermi level. We shall extract the various hopping integrals which in turn could be related to the exchange interactions that we calculated in the preceding section.

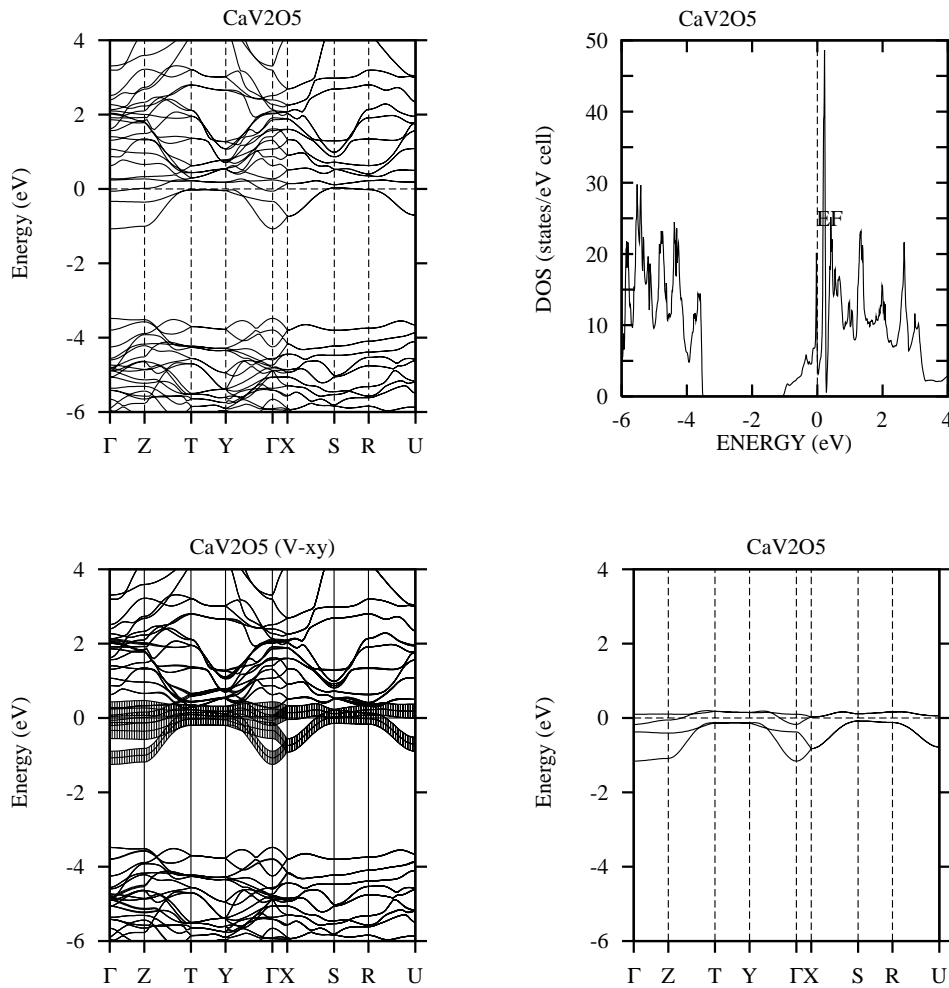


Figure 5. Top left: TBLMTO-ASA energy bands; top right: the density of states; bottom left: the xy -orbital-projected band structure; and bottom right: the band structure of the effective four-band model for CaV_2O_5 .

Top left and top right in figure 5 we show the energy bands and density of states (DOS) respectively for CaV_2O_5 . The bands are plotted along the various high-symmetry lines [19] of the Brillouin zone corresponding to the primitive orthorhombic lattice. Similarly, top left and top right in figure 6 we show the energy bands and density of states respectively for MgV_2O_5 . The bands are now plotted along the various directions of the Brillouin zone corresponding to a base-centred orthorhombic lattice. All the energies in the figures are measured with respect to the Fermi levels of the respective compounds. In both compounds the bands below -3 eV have predominantly oxygen 2p character and are separated from the V d complex by a gap. From -1 eV to 3 eV the bands with V 3d character are spread. Bottom left in figure 5 and figure 6 we show the band structure of CaV_2O_5 and MgV_2O_5 respectively but projecting out the V xy -orbital character, so that the fatness in each figure is proportional to the character of the V xy -orbital (where x runs along the rung and y runs along the leg of the two-dimensional ladder system) in the wavefunction. The orbital analysis of the bands or the so-called *fat*

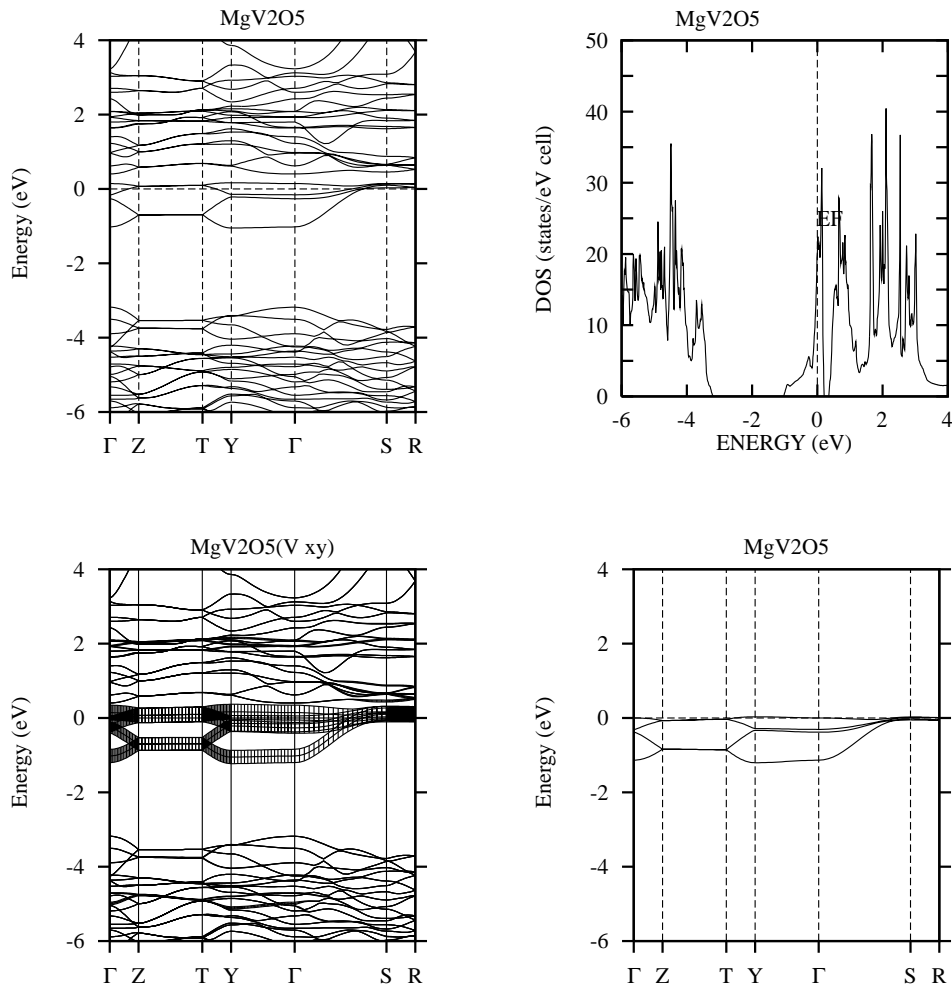


Figure 6. Top left: TBLMTO-ASA energy bands; top right: the density of states; bottom left: the xy -orbital-projected band structure; and bottom right: the band structure of the effective four-band model for MgV_2O_5 .

bands confirms that the four lowest bands of the V 3d manifold are predominantly formed by V xy -orbitals, consistently with the crystal-field arguments presented in the previous section. The crystal-field splitting between the xy -orbital and other 3d orbitals is so strong that in the LDA band structure, particularly for MgV_2O_5 , the xy -bands are separated from the rest of the V 3d bands by a small energy gap as can be seen top right in figure 5. With one subset of energy bands so well separated from the rest, one can hope that a tight-binding model with a single xy -orbital per V site (i.e. a four-band model, because there are four V atoms in the unit cell) will provide a good approximation to the full band structure close to the Fermi level.

In order to achieve this, the third-generation TB-LMTO downfolding method [7] has been employed to obtain a four-band effective V–V model. The crucial difference between the traditional LMTO method and the improved third-generation TB-LMTO method lies in the description of the interstitial. In the traditional LMTO method, the energy-independent basis set was constructed in such a way that it was correct to first order within the MT spheres and to

zeroth order in the interstitial. In order to remedy this inconsistency one has to resort to atomic sphere approximation (ASA), so one replaces the MT spheres by overlapping space-filling spheres. In contrast, in the new version, the energy dependence of the interstitial is treated on an equal footing with the MT spheres, so the single-particle energies ϵ_i obtained from the Hamiltonian and overlap matrices in the new basis set are energetically more accurate. The error in the single-particle energies in the new method is proportional to $(\epsilon_i - \epsilon_v)^4$ (where ϵ_v is the energy of linearization), compared to single-particle energy errors of order $(\epsilon_i - \epsilon_v)^2$ in previous versions. This in turn leads to a more compact and accurate formalism which makes it possible to extract an orthogonal tight-binding Hamiltonian even in the presence of downfolding, and also includes the non-ASA correction, i.e. the combined correction.

The energy bands obtained from the effective four-band V–V model are shown bottom right in figure 5 and figure 6 respectively for CaV_2O_5 and MgV_2O_5 . It can be seen that the agreement with the LDA bands shown top left in figure 5 and figure 6 is remarkable. At this point it may be remarked that the downfolded orbitals are not thrown away but are included in the tails of the active LMTOs which are retained in the basis, i.e. in the tails of the V_{xy} orbitals. In contrast to the fitting procedure often used to obtain tight-binding Hamiltonians, the present method is deterministic and is free from adjustable parameters, and also provides information about the wavefunctions. The Fourier transform of the downfolded Hamiltonian $H(k) \rightarrow H(R)$ gives the effective hopping parameters for both compounds. Such an effective Hamiltonian is long ranged and has been called the physical Hamiltonian. We list in table 3 all the hopping integrals which are relevant to understanding the various exchange couplings presented in section 3. It can be seen from table 3 that, analogously to the exchange couplings, the rung and leg hoppings of CaV_2O_5 are highly anisotropic while all the hoppings are of comparable strength in MgV_2O_5 .

Table 3. Calculated hopping parameters in an effective four-band V–V model (in eV). The notation for the hopping parameters is the same as that for the exchange interactions.

	CaV_2O_5	MgV_2O_5
t_1	0.076	0.128
t_2	0.252	0.114
t_3	0.101	0.109
t_4	0.056	0.069

The exchange interaction parameter for the Hubbard model with strong Coulomb interaction can be estimated as $J = 4t^2/U$, where t is the hopping parameter and U is the Coulomb interaction. For CaV_2O_5 the hopping along the rung of the ladder is 0.252 eV and $U = 3.6$ eV, which gives $J = 816$ K (our LDA + U calculation gives $J = 608$ K). The ratio of the rung and leg exchange parameters (J_2/J_3) is equal to 4.98 while the ratio of the squares of the hopping parameters calculated in the downfolding procedure is equal to 6.25, confirming the strong anisotropy of the exchange couplings in CaV_2O_5 . The rung and leg hopping parameters for MgV_2O_5 are nearly equal, which again agrees with the LDA + U estimate for the exchange couplings in MgV_2O_5 .

The hopping integrals extracted from the effective four-band V–V model are consistent with the exchange couplings calculated from the LDA + U method in the previous section. We shall now employ the downfolding method to explore the reason for the exchange as well as hopping integrals along the rung and leg for CaV_2O_5 being so different in comparison to those for MgV_2O_5 , although for both compounds the vanadium oxide planes have nearly the same geometry.

It has been argued [20] that at least the rung- J_2 and the leg- J_3 exchange integrals are

mediated by the super-exchange mechanism through the O 2p orbitals and that the size of this exchange integral primarily depends on the hopping integral t_{pd} for hops between the xy -orbital of the vanadium and the p orbitals of the oxygen. According to the canonical band theory the structural difference between the two compounds should account for the observed differences. It should be noted that such super-exchange processes are explicitly taken into account in our effective V–V model in the process of downfolding.

Moreover in contrast to the case for cuprates, where the effective hopping predominantly originates from the σ -overlap of the Cu 3d orbitals with the oxygen 2p orbitals, for the vanadates the π -overlap with the oxygen orbitals and the direct V 3d–3d overlap could be of the same order of magnitude.

The preceding discussion suggests that a model with an oxygen p_x orbital along the leg and an oxygen p_y orbital along the rung in addition to the V xy -orbitals should be a good starting point for attempts to gain an understanding of these materials. Such a model Hamiltonian with more orbitals is usually short ranged and will be referred to as a chemical Hamiltonian, as it is expected to possess the necessary degrees of freedom to ensure that its tight-binding parameters behave in a meaningful way when the structure is deformed and when we proceed to study similar materials. Accordingly, we have extracted all the hoppings in a tight-binding Hamiltonian where in the basis we have retained only oxygen p_x orbitals along the leg, oxygen p_y orbitals along the rung, and all the V_{xy} orbitals. All other orbitals were downfolded. Our calculation shows that the V_{xy} –O_p hoppings (t_{pd}) are consistent with the prediction of the canonical band theory. In fact the ratio t_{pd}^{rung} for CaV_2O_5 to MgV_2O_5 is given as 1.21 according to canonical band theory while our downfolding method yields 1.11. Furthermore, in this model the anisotropy between the rung and leg hopping is absent in CaV_2O_5 . However, for MgV_2O_5 the direct V_{xy} – V_{xy} hopping along the rung is found to be very small in comparison to that for CaV_2O_5 . This is not consistent with canonical band theory as the V–V distances in CaV_2O_5 are smaller in comparison to MgV_2O_5 (see table 1). In order to overcome this problem we tried to include more orbitals in the basis, as has been done for the high- T_c cuprates [21] and the ladder cuprate SrCu_2O_3 [22]; however, the direct V–V as well as V–O hoppings remained nearly the same as in the V–O model discussed above. The reason that a chemical Hamiltonian could not be defined for the vanadates on the same footing as for the cuprates may be the complicated geometry of the vanadates. As a consequence, the orbitals are deformed in the process of downfolding, thereby ruling out the validity of the simple canonical band theory.

However, in this paper we have adopted the following strategy to overcome this problem. Chemical intuition suggests that the anisotropy of the leg and the rung exchange interactions in CaV_2O_5 and its absence in MgV_2O_5 may be attributed to the following: (a) the chemical composition of the compounds—particularly the smaller ionic radii of Mg in comparison to Ca; the (b) difference in crystal structure of these materials.

In order to explore these effects we have considered three different models for CaV_2O_5 and have calculated the exchange interactions by the LDA + U method, as explained earlier, and all the hopping parameters for the effective four-band V_{xy} – V_{xy} model. In the first model, referred to as model 1, Ca is replaced with Mg in CaV_2O_5 , to examine whether the chemical composition plays any role in determining the anisotropy of the exchange interactions as well as hoppings in these materials. In order to explore the role of crystal structure we have considered the following two models. Model 2 is the same as model 1 except that now the V–V and V–O distances are changed so that they are equivalent to those in MgV_2O_5 . Finally, in model 3 we have not only changed the V–V and V–O distances but also the V–O–V angles are changed so that they are the same as in MgV_2O_5 . The results of our calculation for the exchange couplings as well as hoppings for the effective V–V model are summarized in table 4.

From table 4 we reach the following conclusion. The calculation of the exchange coupling

Table 4. Calculated exchange couplings (in K) and hopping parameters (in eV) for the models as described in the text.

System	J_2	J_3	t_2	t_3
Model 1	320	92	0.169	0.065
Model 2	466	57	0.199	0.045
Model 3	24	143	0.053	0.107

and the hopping parameters in model 1 suggests that the change in chemical composition, i.e. replacing Ca with Mg, does not influence the leg and rung anisotropy as seen in CaV_2O_5 . Similarly, from model 2 we conclude that bond lengths do not play any role in determining the observed anisotropy between the leg and rung exchange interactions as well as hoppings in CaV_2O_5 . However, calculations based on model 3 clearly show that as soon as the V–O–V angles are changed the exchange couplings as well as the effective hopping parameters are influenced appreciably. In this case, the rung exchange coupling and also the bare hopping are even smaller in comparison to the case for the leg. We obviously recover the values obtained for MgV_2O_5 as soon as the primitive orthorhombic stacking is changed to base-centred orthorhombic stacking. These calculations suggest that the difference in tilting angle of the VO_5 pyramids is the cause for the strikingly different magnetic behaviour of the two vanadates considered here.

5. Conclusions

We have used the LDA + U method to compute the exchange couplings in the layered vanadate compounds CaV_2O_5 and MgV_2O_5 . Our calculation shows that a strong anisotropy exists between the rung and leg exchange couplings for CaV_2O_5 , thus making it a system of weakly coupled dimers along the rung with strong interaction inside the dimer, characterized by a large spin gap. On the other hand, the rung and leg exchange couplings are found to be of comparable strength for MgV_2O_5 , making it a small-spin-gap system. We have applied the recently developed third-generation LMTO downfolding method and subsequently Fourier transformed the downfolded Hamiltonian to extract the tight-binding parameters for hopping between effective V_{xy} – V_{xy} orbitals for CaV_2O_5 and MgV_2O_5 , as well as for three different model systems. We conclude that the stronger *tilting* of the VO_5 pyramids in the MgV_2O_5 crystal structure in comparison to CaV_2O_5 is the reason that the exchange interactions along the rung and leg are nearly identical in MgV_2O_5 while they are anisotropic in CaV_2O_5 , leading to the strikingly different magnetic properties of these materials.

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