Direct exchange in the edge-sharing spin-1/2 chain compound MgVO$_3$

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Bandstructure calculations with different spin arrangement for the spin-chain compound MgVO$_3$ have been performed, and paramagnetic as well as magnetic solutions with ferro- and antiferromagnetically ordered chains are found, the magnetic solutions being by 0.22 eV per formula unit lower than the paramagnetic one. The orbital analysis of the narrow band crossing the Fermi level in the paramagnetic solution reveals that the band has almost pure vanadium $3d$ character, the lobes of the relevant $d$-orbitals at the neighboring in-chain sites being directed towards each other, which suggests direct exchange. The tight-binding analysis of the band confirms the strong exchange transfer between neighboring in-chain V-ions. Besides, some additional superexchange transfer terms are found, which give rise both to in-plane coupling between the chains and to frustration, the dominant frustration occurring due to the interchain interactions.

Spin chains and ladders are of fundamental interest for solid state physics due to their peculiar properties. In the last years many spin-chain compounds were found, mostly cuprates and vanadates. There one can distinguish between the corner-sharing compounds with a 180° (T)ransition metal–(L)igand–T bond (Sr$_2$CuO$_4$) and the edge-sharing compounds with a 90° T–L–T bond (Li$_2$CuO$_2$, CuGeO$_3$, MgVO$_3$). In cuprates the relevant $d$-orbitals are directed towards the ligand ions, which results in a strong antiferromagnetic superexchange interaction for a 180° T–L–T bond and a weaker ferromagnetic coupling for a 90° T–L–T bond according to the Goodenough-Kanamori-Anderson (GKA) rules. Deviations from the GKA rules are known for CuGeO$_3$ due to the presence of side groups.

Recently, the compound MgVO$_3$ was proposed as a new candidate for a model spin-chain system and magnetic susceptibility measurements were presented. The data suggest short range antiferromagnetic spin correlations with the constant of the high-temperature Curie-Weiss law $\theta \approx -100$ K. The data were analyzed within a 1D spin-1/2 Heisenberg model with the nearest neighbor $J_1$ and the next nearest neighbor $J_2$ exchange couplings and a frustration $\alpha = J_2/J_1$ close to the critical value $\alpha_c = 0.24$ was found. Here we present bandstructure calculations for this compound and a corresponding orbital and tight-binding (TB) analysis.

The base-centered orthorhombic crystal structure of MgVO$_3$ was determined by Bouloux et al. and is shown in Fig. 1. It consists of edge-sharing VO$_2$ chains running along the $y$-direction which are coupled in $x$-direction by V–O–O–V bonds. For a convenient presentation of the orbital analysis the coordinate system is rotated 90° about the $x$-axis against the standard one, so that the space group reads as Bm2$_1$b instead of Cmc2$_1$ given in Ref.

![Crystal structure of MgVO3](image)

FIG. 1. Crystal structure of MgVO$_3$. The dashed lines depict the Bravais unit cell. The lattice parameters of the cell are $a = 5.243$ Å, $b = 5.293$ Å, $c = 10.028$ Å.

One notes a slight tilting of the VO$_5$ pyramids out of the $z$-direction and an asymmetric coordination of V and O1 ions. If one distorts the structure in a way depicted in Table 1, both the tilting and the asymmetry are removed, a center of inversion appears, and the space group becomes Bmmb. All the following results were obtained using the model structure, because this simplification considerably reduces the computational efforts, and, as we have checked for the non-spin-polarized case, the deviation from the result obtained with the real crystal structure is negligible.
The Wyckoff positions of atoms in MgVO$_3$.

| Atom | Real structure | Model structure |
|------|----------------|-----------------|
| Mg   | x   | y   | z   | x   | y   | z   |
| V    | 0   | 0   | 0.2383 | 0   | 0   | 0.2383 |
| O1   | 0.2383 | 0.264 | 0.2330 | 0   | 0   | 0.2330 |
| O2   | 0   | 0.025 | 0.2330 | 0   | 0   | 0.2330 |

The calculation of the bandstructure was performed using the full-potential nonorthogonal local-orbital minimum-basis bandstructure scheme (FPLO) within the local spin density approximation (LSDA). The calculation was non-relativistic, the exchange and correlation potential was taken from Ref. 12. The set of valence orbitals was chosen to be Mg: 3s3p3d, V: 3s3p44s4p3d and O: 2s2p3d. The inclusion of the vanadium 3s3p states turned out to be unavoidable since the V–O distance of about 3.11 a$_0$ is small enough to yield a slight overlap of these states. The oxygen and magnesium 3d orbitals were taken to increase the basis completeness; though being not occupied they contribute to the overlap density. The extent of the basis orbitals, controlled by a confining potential ($r/r_0$)$^4$, was optimized with respect to the total energy.

In our calculation the Bloch state $|k\nu\rangle$ is composed of overlapping atomiclike orbitals $|Lij\rangle$ centered at the atomic sites $j$ in the unit cell $i$ with coordinates $R_{ij}$:

$$|k\nu\rangle = \sum_{Lij} C_{Lij}^k e^{i\mathbf{k}\cdot\mathbf{R}_{ij}} |Lij\rangle,$$

with the normalization condition $\langle k\nu | k\nu \rangle = 1$. $L$ stands for $\{nlm\sigma\}$ denoting the main, orbital, magnetic quantum numbers and the projection of spin, respectively.

We have performed three kinds of computation: one non-spin-polarized and two spin-polarized with collinear and anticollinear spin polarization at the neighboring in-chain vanadium ions. In the last case we assumed ferromagnetic order along the $x$- and $z$-directions. In both spin-polarized calculations we have found magnetic (ferro- and antiferro-) solutions with the total energy being about 0.22 eV per formula unit lower than that of the paramagnetic solution of the non-spin-polarized calculation. The LSDA accuracy does not allow to determine which of the magnetic states is preferable. The magnetic moment $\langle n_\uparrow - n_\downarrow \rangle \mu_B$ of the vanadium ion in both magnetic solutions is close to the saturated value $1 \mu_B$. The magnetic moments of the other ions are much smaller, the only appreciable one occurs at apex oxygen (O2) having a value of about 0.05 $\mu_B$ and being directed opposite to the moment of the neighboring vanadium ion.

The results of all three calculations are presented in Fig. 2. The paramagnetic solution has metallic character with a half-filled conduction band at the Fermi level, whereas the band splits in two in the magnetic solutions and an insulator gap opens, being about 0.5 eV and

![FIG. 2. Band structure and density of states of MgVO$_3$ for the paramagnetic (a), ferromagnetic (b) and antiferromagnetic (c) solutions. The symmetry point coordinates of the $B$-base centered orthorhombic Brillouin zone are given in units $\pi(2/a, 1/b, 2/c)$. The majority and minority (tinier dots and shaded DOS) spin parts are shown.](image-url)
0.8 eV in ferro- and antiferromagnetic cases, respectively. However, it can be expected that the real gap is caused mainly by the electron correlation and is considerably larger than that one produced by the magnetic ordering. The correlation gap should persist in the paramagnetic case as well.

For a deeper understanding of the electronic structure we have performed an orbital analysis for the paramagnetic case. The weight \( W_{Lj}^{\nu} \) of the orbital \( |Lj\rangle \) in the Bloch state \( |k\nu\rangle \) (Eq. 2) was taken as

\[
W_{Lj}^{\nu} = \sum_i |C_{Lij}|^2.
\] (2)

The sum of all weights \( \sum_{Lj} W_{Lj}^{\nu} \) is approximately unity, with some deviation due to the nonorthogonality of the basis orbitals. Actually the orbital weights were normalized with respect to the sum.

According to the analysis, the valence bands consist of a lower oxygen 2p-orbital complex which is separated by 3 eV from upper vanadium 3d-orbitals (cf. Fig. 3). The 3d-orbitals are split according to the standard crystal field rules. At (0,1,0) their energy rises in the order: \( d_{x^2-y^2}, d_{yz}, d_{xz}, d_{3z^2-r^2}, d_{xy} \). Only the lowest 3d_{x^2-y^2}-orbital is partially occupied, being half-filled with two electrons per two vanadium atoms in the primitive unit cell. The corresponding band (see Fig. 3) is very narrow having a width of only 0.8 eV. The weight of the V: 3d_{x^2-y^2} orbital in the band is larger than 70 percent, but there are considerable contributions up to 20 percent from the O1: 2p_\perp and the V: 3d_{yz} orbitals, as well as smaller contributions from some other orbitals. Comparing the situation with that in cuprates having edge-sharing CuO_2 chains (Li_2CuO_2 or CuGeO_3) one observes an important distinction: in the cuprates the relevant Cu: 3d-orbital is directed towards the oxygen ions, whereas in the present case it is directed towards the neighboring vanadium ions. It implies an indirect superexchange mechanism via the intermediate ligand in the cuprates but probably a dominant direct exchange process between neighboring vanadium ions and a much smaller superexchange hopping to the second in-chain neighbor in MgVO_3.

Let us note that the different coordination of the relevant 3d-orbital in vanadates and cuprates with similar crystal structure has to be a rather common feature, because in vanadates the energetically lowest 3d-orbital is half-filled in contrast to the highest one in cuprates.

The coupling between the neighboring chains occurs mainly in the \( xy \)-plane via the intermediate O1: 2p_\perp orbitals. This is manifested by the strong dispersion along the \((k_x, 0, 0)\) direction (see Fig. 3) of the lower part of the band, which has a remarkable contribution from the orbital, whereas the upper part having a contribution only from the O1: 2p_\parallel orbital is almost dispersionless. Fig. 4 showing the relevant orbitals at the \( \Gamma \)-point illustrates the interchain coupling via \( \sigma \)-bonds of neighboring O1: 2p_\perp orbitals.

To quantify the result a TB analysis has been performed for the relevant band of the paramagnetic solution. The hopping processes to the nearest \((t_{1y})\) and the next nearest \((t_{2y})\) in-chain neighbors, as well as two hopping processes \((t_x, t_{xy})\) to the next chain and one \((t_{xyz})\) possible coupling in the \( z \)-direction were taken into account:

\[
E_0 - E_k = 2t_{1y} \cos \frac{b}{2} + 2t_{2y} \cos \frac{b}{2} + 2t_x \cos \frac{a}{2} \cos \frac{b}{2} \cos \frac{c}{2} + 4t_{xy} \cos \frac{a}{2} \cos \frac{b}{2} + 8t_{xyz} \cos \frac{a}{2} \cos \frac{b}{2} \cos \frac{c}{2},
\]

yielding the parameters (in meV): \( t_{1y} = 125, t_{2y} = 20...26, t_x = 50, t_{xy} = 20 \) and a tiny value of 3 for \( t_{xyz} \). The data confirm that the ratio \( t_{2y}/t_{1y} \), a measure for the frustration in the chain direction, is much smaller than the corresponding value for CuGeO_3 and Li_2CuO_2.

It should be noted that the parameter \( t_{1y} \) is much larger than the corresponding inter-ladder hopping in NaV_2O_5.

![FIG. 3. Dispersion (a) and orbital weights of the upper (b) and lower (c) parts of the band crossing the Fermi level in the paramagnetic solution. The coordinates of \( k \)-points are given in the same units as in Fig. 2](image-url)
given in Ref. 15, probably due to a mutual compensation of different transfer paths in the ladder compound.

An estimate of the corresponding exchange integrals of the effective Heisenberg Hamiltonian

\[ \hat{H} = \frac{1}{2} \sum_{ij} J_{ij} S_i S_{i+j} \]

can be performed in the one-band Hubbard description, which gives an antiferromagnetic exchange of roughly \( J = 4t_2^2/U \) with a value of \( U \) still to be determined. Using the experimental value of \( J_{1y} \approx 10 \text{ meV} \) given in Ref. 15 one gets \( U = 6.25 \text{ eV} \) which seems to be slightly overestimated. Most probably, additional ferromagnetic processes (possibly via the \( 3d_{yz} \) orbital or indirect processes via oxygen) have to be included to improve the estimate. Our TB analysis suggests a rather large value for \( J_x \). It gives two-dimensional antiferromagnetic order with the frustration terms \( J_{2y} \) and \( J_{xy} \) (see Fig. 3). Though \( t_{2y} \) and \( t_{xy} \) are of nearly the same value, due to the larger coordination number, \( J_{xy} \) dominates. In a simple mean field approach one can define an effective frustration exchange \( J_{\text{eff}} = 2J_{xy} + J_{2y} \) yielding an effective frustration \( J_{\text{eff}}/J_{1y} \) of roughly 0.1 which is a very preliminary analysis, however.

Thus, we have found that the \( \text{VO}_2 \) chains of \( \text{MgVO}_3 \) have indeed a spin-1/2 structure. In contrast to the crystallographically similar edge-sharing cuprates the relevant \( 3d \) orbital is directed towards the nearest in-chain transition metal (V) ions. It suggests a direct antiferromagnetic exchange process between the neighboring in-chain spins. A similar process was proposed earlier for the inter-ladder exchange coupling in \( \text{MgV}_2\text{O}_6 \). The importance of the direct vanadium \( d-d \) transfer was also anticipated in Ref. 17 for \( \text{CaV}_2\text{O}_6 \), a compound with V-V distance slightly larger (3.00 Å) than in \( \text{MgVO}_3 \) (2.96 Å), where a value of 80 meV for the transfer was reported. Besides the direct exchange we have found also some additional superexchange terms which give rise to the coupling between the chains in the \( x \)-direction and to the frustration. The dominant frustration occurs between the neighboring chains in contrast to the naive picture of the frustration due to the next-nearest in-chain neighbor superexchange. It suggests that the experimental data require an analysis in the framework of a two- rather than a one-dimensional Heisenberg model.

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1. Dagotto, E. and Rice, T.M., Science 271 (1996) 618.
2. Kojima, K.M. et al. Phys. Rev. Lett. 55 (1987) 1787.
3. Mizuno, Y. et al., Phys. Rev. B 57 (1998) 5326.
4. Morré, E., Geibel, C. and Löw, U. to be published.
5. Rosner, H. et al., Phys. Rev. B 56 (1997) 3402.
6. Anderson, P.W., Solid State Phys. 14 (1963) 99.
7. Geertsma, W. and Khomskii, D. Phys. Rev. B 54 (1996) 3011.
8. Okamoto, K. and Nomura, T., Phys. Rev. Lett. A 169 (1992) 433.
9. Bouloux, J.-C., Milosevic, I. and Galy, J., J. Sol. State Chem. 16 (1976) 393.
10. International Tables for Crystallography, Kluwer Academic Publishers, 1995.
11. Köpernik, K. and Eschrig, H., Phys. Rev. B 59 (1999) 1743.
12. Perdew, J. P. and Zunger, A., Phys. Rev. B 23 (1981) 5048.
13. Weht, R. and Pickett, W.E., Phys. Rev. Lett. 81 (1998) 2502.
14. Rosner, H., Hayn, R. and Drechsler S.-L., Physica B 259-261 (1999) 1001.
15. Smolinski, H. et al., Phys. Rev. B 57 (1998) 5326.
16. Millet, P. et al., Phys. Rev. B 57 (1998) 5005.
17. Pickett, W.E., Phys. Rev. Lett. 79 (1997) 1746.