Electronic structure of the zigzag spin-chain compound \( \text{In}_2\text{VO}_5 \)

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Band structure calculations within the local spin-density approximation are presented in order to investigate the electronic and magnetic properties of the zigzag spin-chain compound \( \text{In}_2\text{VO}_5 \). The essential structural feature of the system is a double chain of \( \text{VO}_6 \)-octahedra, which leads to competing intrachain and interchain magnetic couplings. Frustration of the spin-chains is expected for the proposed antiferromagnetic ordering at low temperatures. However, the band calculations indicate that the experimental room temperature crystal structure is incompatible with antiferromagnetism. Both the intrachain and interchain coupling is found to be ferromagnetic.

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Magnetism in low-dimensional quantum spin systems results in fascinating physical properties when the spin ordering is frustrated due to geometrical restrictions. In this context, the \( S = 1/2 \) antiferromagnetic zigzag spin-chain gives rise to one of the most fundamental model systems for analyzing the interplay of frustration and magnetism. Recently, \( \text{In}_2\text{VO}_5 \) has been put forward for consideration as a promising candidate for a frustrated zigzag spin-chain. Vanadium oxides in general are very susceptible to electronic ordering phenomena, see [1, 2, 3], for instance, and the references given there. To be more specific, the essential structural feature of \( \text{In}_2\text{VO}_5 \) is a double chain of corner sharing \( \text{VO}_6 \)-octahedra along the crystallographic \( b \)-axis. As indium realizes the oxidation state \( \text{In}^{3+} \), the vanadium ions are left with a single electron in the 3d shell. This formal \( V^{4+} \) valence with a 3d\(^1 \) electronic configuration comes along with \( S = 1/2 \) spins at the vanadium sites, separated by non-magnetic oxygen sites. Because of nearest and next-nearest neighbour V-V interactions of the same order of magnitude, competence between the intrachain and interchain exchange coupling is typical for \( \text{In}_2\text{VO}_5 \).

The compound crystallizes in the simple orthorhombic space group \( Pnma \), where a unit cell comprises four formula units. Senegas et al. [4] have obtained the lattice parameters \( a = 7.232 \text{ Å} \), \( b = 3.468 \text{ Å} \), and \( c = 14.82 \text{ Å} \) by means of single crystal x-ray analysis at room temperature. Figure illustrates the spacial arrangement of the zigzag VO-chains. The coordination polyhedron of the magnetic V sites is a distorted O-octahedron with one strongly elongated VO-bond of length 2.23 Å. This bond connects two adjacent VO-chains, therefore giving rise to the characteristical double chain geometry. The VO-bond in trans-position accordingly is shortened to 1.76 Å. Moreover, the intrachain bond length amounts to 1.81 Å in both directions and the remaining VO-bonds in the equatorial plane of the coordination polyhedron have lengths of 2.01 Å and 2.03 Å. All V sites are crystallographically equivalent, as are the intrachain O sites. Within the zigzag VO-chains we have V-O-V bond angles of 146°, thus considerable deviations from a straight line configuration. In contrast, the V-O-V bond angles between V sites in adjacent chains amount to only 107°. Nearest neighbour magnetic sites therefore are located in different VO-chains, whereas intrachain V sites are next-nearest neighbours.

Sign and strength of the magnetic coupling constants in \( \text{In}_2\text{VO}_5 \) very recently have been analyzed by Volkova [5] based on a phenomenological theoretical method for quantitatively estimating the magnetic coupling in low-dimensional crystalline compounds. The only input into the calculation is the crystal structure. This crystal chemical approach results in an antiferromagnetic nearest-neighbour interaction given by the coupling constant \( J_1 = -0.9 \text{ mRyd} \). Competing magnetic interaction along the zigzag VO-chains is likewise antiferromagnetic, with coupling constant \( J_2 = -1.6 \text{ mRyd} \). Despite two paths for the nearest neighbour exchange and a single path for the intrachain exchange, see figure, the next-nearest neighbour magnetic coupling therefore is found to dominate. Furthermore, since the ratio \( J_2/J_1 = 1.68 \) exceeds the Majumdar-Ghosh point 0.5, the zigzag spin-chains in \( \text{In}_2\text{VO}_5 \) are expected to be frustrated.

The following electronic structure results for \( \text{In}_2\text{VO}_5 \) rely on the scalar-relativistic augmented spherical wave (ASW) method. The implementation in use particularly accounts for the non-spherical contributions to the charge density inside the atomic spheres. The structural

FIG. 1: (Color online) Schematic structure of the zigzag VO-chains in \( \text{In}_2\text{VO}_5 \). The magnetic V sites are surrounded by distorted O-octahedra, sharing corners along the chains.
input for the calculation is taken from Senegas et al. [4]. For a correct representation of the crystal potential in voids of the In$_2$VO$_3$ structure the physical spheres have to be complemented by additional augmentation spheres at carefully selected interstitial sites. It turns out that it is sufficient to dispose 84 additional spheres from 15 crystallographically inequivalent classes in order to keep the linear overlap of the physical spheres below 15% and the overlap of any pair of spheres below 20%. Since we have 32 physical spheres, the unit cell entering the calculation thus comprises 116 augmentation spheres in total. The basis set taken into account in the secular matrix consists of In 5s, 5p, 4d, V 4s, 4p, 3d, and O 2s, 2p states, as well as states of the additional augmentation spheres. During the course of the band structure calculation the Brillouin zone is sampled with an increasing number of up to 56 k-points in the irreducible wedge, which ensures convergence of the results with respect to the fineness of the k-space grid. For the exchange-correlation functional the Vosko-Wilk-Nusair parametrization is used. As long as the augmentation spheres are selected carefully and the crystal structure is not altered, the ASW method is highly reliable for the comparison of magnetic energies.

We start the discussion of the electronic structure of In$_2$VO$_3$ by addressing results of a spin-degenerate band structure calculation. They allow us to study general issues concerning the anisotropy of the electronic states, the chemical bonding, and hybridization effects. Afterwards we will investigate the magnetic coupling by spin-polarized calculations for various spin patterns. Figure 2 shows the band structure for the spin-degenerate case along selected high symmetry lines in the first Brillouin zone of the simple orthorhombic lattice, where the high symmetry points are defined by the standard reciprocal lattice vectors $\Gamma = (0, 0, 0)$, $X = (\frac{1}{2}, 0, 0)$, $S = (\frac{1}{2}, \frac{1}{2}, 0)$, $Y = (0, \frac{1}{2}, 0)$, $Z = (0, 0, \frac{1}{2})$, $U = (\frac{1}{2}, 0, \frac{1}{2})$, $R = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and $T = (0, \frac{1}{2}, \frac{1}{2})$. In the vicinity of the Fermi energy, we have several electronic bands revealing little dispersion throughout the first Brillouin zone. Because these bands originate from the V 3d states, they are responsible for a remarkable peak in the V 3d density of states (DOS), compare the DOS curves in figure 2. In the energy range shown, we have almost only contributions from the V 3d and O 2p states. Fully occupied In 4d bands give rise to a pronounced structure around $-15$ eV, with respect to the Fermi level.

The gross features of the partial V 3d and O 2p DOS are typical for compounds based on VO$_6$-octahedra. As to be expected from a molecular orbital picture, we can identify two groups of bands in the energy ranges from $-8.5$ eV to $-2.8$ eV and from $-0.2$ eV to 4.2 eV. Interaction between V 3d and O 2p atomic orbitals leads to bonding and antibonding molecular states. The bonding bands are fully occupied, whereas the antibonding bands cross the Fermi level and cause In$_2$VO$_3$ to be a metal at room temperature. Even though the bonding and antibonding states are dominated by oxygen and vanadium contributions, respectively, non-vanishing admixtures of the other states are present in figure 2. They trace back to significant VO-hybridization, particularly between orbitals mediating $\sigma$-type overlap.

For investigating the magnetic coupling in In$_2$VO$_3$, we have to consider the following three spin patterns, since nearest and next-nearest neighbour exchange interaction is relevant. First, we assume the magnetic coupling to be ferromagnetic both along the VO-chains and between neighbouring chains. Afterwards, we assume either the intrachain or the interchain coupling to be antiferromagnetic, while keeping the other coupling ferromagnetic.

### Table I: Comparison of the energy gain (per V site) due to the exchange coupling for various spin patterns.

|        | intrachain coupling | interchain coupling | energy gain |
|--------|---------------------|---------------------|-------------|
| fe     | fe                  | 12 mRyd             |
| fe     | af                  | 10 mRyd             |
| af     | fe                  | 4 mRyd              |

![Figure 2: (Color online) Band structure and partial V 3d and O 2p DOS (per atom), as resulting from a spin-degenerate calculation.](image-url)
each case, spin-polarized band structure calculations result in a lowering of the total energy as compared to the spin-degenerate solution. Values for the energy gain per magnetic site are summarized in table I. The largest energy gain of 12 mRyd is obtained when both the nearest and next-nearest neighbour exchange interaction is ferromagnetic. With respect to this value, intrachain and interchain antiferromagnetic coupling raises the energy by 2 mRyd and 8 mRyd, respectively. The magnetic ground state of In$_2$VO$_5$ hence is found to be ferromagnetic, i.e. the room temperature crystal structure of Senegas et al. is incompatible with antiferromagnetism within the VO-chains as well as between the chains.

We next study the effects of the intrachain magnetic coupling on the electronic structure of ferromagnetically coupled VO-chains. Partial V 3d spin-majority and spin-minority densities of states for ferromagnetic and antiferromagnetic exchange along the chains are shown in figures 3 and 4. The width of the spin-majority bands in figure 3 amounts to 4.8 eV. It therefore is about 0.4 eV larger than for the spin-degenerate bands, see figure 2, whereas the width of the spin-minority bands hardly alters. In contrast, the spin-majority and spin-minority band widths are rather similar in figure 4. While for ferromagnetic intrachain coupling the spin-minority group of states is observed at higher energies, leaving only V 3d spin-majority states occupied, both spin components contribute at the Fermi level for antiferromagnetic coupling. As a consequence, the local V magnetic moment accumulates to only 0.71 $\mu_B$ in the latter case. Oxygen magnetic moments are negligible. On the contrary, the ferromagnetic intrachain coupling results in magnetic moments of 0.92 $\mu_B$ for the V and 0.05 $\mu_B$ for the intrachain O sites, which sum up to 4 $\mu_B$ per unit cell. Due to a strong spin splitting of nearly 0.8 eV, see figure 3, a large number of occupied states is shifted to lower energies, paving the way for the ferromagnetic ground state.

In conclusion, electronic structure calculations using

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**FIG. 3:** (Color online) Partial V 3d spin-majority (top) and spin-minority (bottom) DOS (per atom) for ferromagnetic intrachain coupling.

**FIG. 4:** (Color online) Partial V 3d spin-majority (top) and spin-minority (bottom) DOS (per atom) for antiferromagnetic intrachain coupling.
density functional theory indicate that the experimental room-temperature crystal structure of the zigzag spin-chain compound In$_2$VO$_5$ is incompatible with both antiferromagnetic intrachain and interchain coupling. Ferromagnetism is stabilized instead, which contradicts the crystal chemical estimates by Volkova [5]. This discrepancy probably traces back to hybridization between the V 3$d$ and O 2$p$ states, as reflected by remarkable oxygen magnetic moments. Nevertheless, the antiferromagnetic coupling likewise comes along with energy gain as compared to the non-magnetic solution. Because of narrow V 3$d$ bands at the Fermi energy, see figure 2 electronic correlations beyond the local density approximation can play a role and further stabilize antiferromagnetic interaction. However, this seems not to be the case here, as recent experiments point at a transition from ferromagnetic to antiferromagnetic exchange at low temperature, accompanied by structural alterations [8]. Since strong coupling of the electronic system to the crystal lattice is typical for transition metal oxides [9], slight changes in the crystal structure may induce relevant modifications of the magnetic exchange. A large variety of phase transitions is known for compounds with octahedrally coordinated transition metal atoms. The vanadium and titanium Magnéli phases, for example, are subject to metal-insulator transitions accompanied by distinct structural alterations [10, 11]. A low temperature structural phase transition in In$_2$VO$_5$ therefore still could cause an antiferromagnetic ground state with frustrated zigzag spin-chains. In order to solve this question, a detailed investigation of the In$_2$VO$_5$ crystal structure is required.

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