Orbital order in \( \text{ZnV}_2\text{O}_4 \)

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In view of recent controversy regarding the orbital order in the frustrated spinel \( \text{ZnV}_2\text{O}_4 \), we analyze the orbital and magnetic groundstate of this system within an \textit{ab initio} density functional theory approach. While \textit{LDA}+\textit{U} calculations in the presence of a cooperative Jahn-Teller distortion stabilize an A-type staggered orbital order, the consideration of relativistic spin-orbit effects unquenches the orbital moment and leads to a uniform orbital order with a net magnetic moment close to the experimental one. Our results show that \textit{ab initio} calculations are able to resolve the existing discrepancies in previous theories and that it is the spin-orbit coupling along with electronic correlations which play a significant role in determining the orbital structure in these materials.

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Correlated electronic systems involving transition metal oxides took the centrestage of condensed matter physics research for the last three decades because of their intriguing, often non-intuitive properties. Transition metal spinel oxides with an additional complexity of a geometrically frustrated lattice provide an exciting ground for the study of several competing interactions among spin, orbital and lattice degrees of freedom\(^5\). Besides being of fundamental interest, spinels have been also proposed for spintronics applications\(^6,7,8\). In the present work on \( \text{ZnV}_2\text{O}_4 \) we investigate the effect of competing spin, orbital and lattice degrees of freedom and show that density functional calculations provide an adequate and realistic ground to establish the dominant mechanism driving the orbital order in vanadium spinels.

The orbital order in \( \text{ZnV}_2\text{O}_4 \) as well as in other vanadium spinels such as \( \text{MgV}_2\text{O}_4 \) and \( \text{CdV}_2\text{O}_4 \) is presently a subject of considerable debate\(^6\). In order to understand the behavior of these compounds, various groups\(^5,7,8\) have proposed alternative microscopic mechanisms which predict different orbital patterns. The ongoing debate has its origin in the complex nature of these systems with competing spin, orbital and lattice degrees of freedom. These systems have \( \text{V}^{3+} \) ions in a spin 1 state characterized by double occupancy of the triply degenerate \( t_{2g} \) \((d_{xy}, d_{xz}, d_{yz})\) orbitals. These partially filled \( t_{2g} \) orbitals leave the orbital degrees of freedom unfrozen opening up the possibility of orbital order. Moreover, the V-sites in the cubic spinel structure form a pyrochlore lattice, which gives rise to frustrated antiferromagnetic interactions among these sites\(^2\). In \( \text{ZnV}_2\text{O}_4 \) the interplay of all these degrees of freedom leads to two successive phase transitions which involve structural, orbital and magnetic changes. At \( T_S = 51 \text{ K} \) \( \text{ZnV}_2\text{O}_4 \) undergoes a structural phase transition where the symmetry is lowered from cubic to tetragonal with a compression of the \( \text{VO}_6 \) octahedron along the \( c \) axis\(^10\) and the system possibly orbital orders. The structural transition also lifts the geometrical frustration of the cubic phase making a way for the second transition at \( T_N = 40 \text{ K} \) which is of magnetic nature and the system orders antiferromagnetically\(^10,11\).

While the antiferromagnetic structure in \( \text{ZnV}_2\text{O}_4 \) at \( T < T_N \) has been unambiguously determined by neutron scattering experiments at low temperatures\(^12\), the nature of the orbital groundstate in the whole temperature range \( T < T_S \) is still unclear. Tsunetsugu and Motome\(^6\) proposed that the Coulomb and exchange interaction between the magnetic ions as expressed in the Kugel-Khomskii Hamiltonian and the coupling to the Jahn-Teller lattice distortion are the driving mechanisms of the consecutive phase transitions. The groundstate orbital order predicted by their model has an alternating singly occupied \( d_{xz} \) and \( d_{yz} \) orbital along the \( c \) direction together with a singly occupied \( d_{xy} \) orbital in all V sites (see Fig. 1, right panel). They showed that this type of orbital order is consistent with the observed antiferromagnetic order at low temperatures\(^11,12\) as well as with the compressed \( \text{VO}_6 \) octahedron in the tetragonal phase\(^10\). But this orbital order breaks the mirror reflections in the planes \((110)\) and \((1\bar{1}0)\) and the diamond glides in the planes \((100)\) and \((010)\) and hence is inconsistent with the spatial symmetry \( I_{41}/amd \) predicted by X-ray scattering experiments on polycrystalline samples\(^10,13\). Recent inelastic neutron scattering data on a single crystal sample\(^7\) seem to suggest though a breaking of the glide symmetry. These results have nevertheless not been further corroborated by other measurements.

Tchernyshyov\(^7\), in a separate theoretical work, considering the fact that \( \text{V}^{3+} \) has a non-negligible orbital moment, proposed a single-ion model where the relativistic spin-orbit coupling plays the dominant role in driving the orbital order in the tetragonal phase. Including the Jahn-Teller effect as a perturbation in his model, Tchernyshyov predicted a uniform (ferro) orbital order with a complex orbital state \( d_{xy} \pm id_{yz} \) at each V-site. This orbital order is consistent with the symmetry \( I_{41}/amd \) since it preserves both mirror and glide symmetries and hence is at odds with the prediction of Tsunetsugu et al.\(^6\). Di Matteo et al.\(^8\) in a subsequent work proposed a third alternative model where both the relativistic spin-orbit coupling and the Kugel-Khomskii model of spin-orbital...
supercexchange are treated on an equal footing. They observed that for intermediate spin-orbit coupling strength the groundstate of the system shows a uniform orbital order compatible with Tchernychyov’s prediction and with the symmetry $I4_1/amd$.

In view of the above mentioned disagreements among the various theoretical models, we analyze in this work the orbital and magnetic groundstate of ZnV$_2$O$_4$ in the tetragonal phase within an ab initio density functional theory (DFT) approach. Our calculations without spin-orbit coupling indicate the presence of a staggered antiferro-orbital order compatible with the spatial symmetry of the tetragonal phase $I4_1/amd$ and we observe that correlation effects are essential for the description of this state. These results agree with the prediction of Tsunetsugu and Motome\cite{tsumun} about the existence of a staggered orbital order except that we obtain a pattern which, contrary to Ref. \cite{tsumun}, is compatible with the underlying $I4_1/amd$ symmetry (see Fig. 1). Inclusion of relativistic spin-orbit effects in our DFT calculations changes though this picture considerably. For moderate to large values of the onsite electronic correlation $U$, a uniform orbital order analogous to the cubic phase $I4_1/amd$ is stabilized. Also, a large orbital moment antiparallel to the spin moment is obtained in the presence of strong onsite correlation which gives rise to a net magnetic moment in close agreement with the experimentally observed one. Finally, we confirm that the antiferromagnetic order observed in neutron scattering experiments\cite{osaka, matsuz} minimizes the ab initio DFT calculations.

Our DFT calculations were performed within the local spin density approximation (LSDA) and the LSDA+U\cite{andersen} approach. The spin-orbit coupling was treated using a scalar-relativistic basis and the second variational method\cite{anderson} (LSDA+U+SO). All calculations were done with the full-potential linearized augmented plane-wave code WIEN2k\cite{wien2k}. The atomic sphere radii were chosen to be 1.96, 1.99 and 1.78 a.u. for Zn, V and O respectively and 40 $\mathbf{k}$ points mesh in the irreducible wedge was considered for Brillouin zone integrations. We used the structure data measured in Ref. \cite{matsuz}.

In Fig. 2 we present the spin polarized density of states (DOS) of Zn, V and O within the LSDA for both spin directions. The V $t_{2g}$ up spin states are partially occupied defining a metallic solution within the LSDA approximation. The calculated magnetic moment per vanadium is 1.48$\mu_B$. The above results show that V$^{3+}$ is in a high spin ($S=1$) state implying strong Hund’s coupling ($J_H$) strength. Due to the $c$-axis compression of the VO$_6$ octahedra, there is a small but finite splitting of the $d_{xy}$-level from the doubly degenerate $d_{xz}/d_{yz}$ level (not shown here).

ZnV$_2$O$_4$ is a Mott insulator, the inclusion of correlation effects are expected to improve on the incorrect metallic solution given by the LSDA approach. It is also well known\cite{wils, novak} that in Mott insulators with orbital degeneracies as in our case, orbital order plays a crucial role in driving any collective Jahn-Teller distortion present in the system. Calculations within the LSDA+U approach -where orbital dependent potentials are included- should then be more appropriate to describe the gap and the possible orbital order in these systems.

In Fig. 3 we present the projected DOS of the V $t_{2g}$ states in the up spin channel calculated within the LSDA+U with $U=5$ eV and $J=0.9$ eV\cite{novak}. Note that the $d_{xy}$ up band now gets completely occupied with one electron and the partially filled doubly degenerate $d_{xz}/d_{yz}$ band observed in LSDA is split into two opening up a gap of 0.4 eV. The second electron now occupies the lower energy up band which has both $d_{xz}$ and $d_{yz}$ character. In Fig. 4 (left panel) we show the corresponding bandstructure. The orbital ground state described below is found to be stable with $U$ values in the range 4 - 6 eV.

We present in Fig. 5 a three-dimensional plot of the spin density of ZnV$_2$O$_4$ calculated within LSDA+U in the range of energies between -2 eV and the Fermi level. This range of energies includes V $t_{2g}$ and O-$p$ states. A close inspection of Fig. 5 reveals that all V ions in the tetragonal spinel structure have one filled $t_{2g}$ orbital in the $ab$-plane ( $d_{xy}$ in the reference frame defined with the $a$, $b$ axes directed along the basal V-O$_6$ bonds and $c$ axis directed along the apical V-O$_6$ bond). This fea-

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FIG. 1: (Color online) Schematic diagram showing the orbital order obtained within LDA+U in this work (left panel) and that proposed in Ref. \cite{tsumun} (right panel).

FIG. 2: Total density of states for Zn, V, and O in both spin up and down channel in LSDA.
the LSDA+U approach.

The second vanadium electron occupies a $t_{2g}$ orbital with symmetry $d_{xz} + d_{yz}$ and $d_{xz} - d_{yz}$ in alternate $ab$-planes respectively along the $c$-direction (please note the four lobes in planes perpendicular to $ab$ in Fig. 4). The $V_4O_4$ cube (Fig. 4 inset) shows two V with the second $t_{2g}$ electron in a $d_{xz} + d_{yz}$ symmetry and two V with the second $t_{2g}$ electron in a $d_{xz} - d_{yz}$ symmetry.

This orbital structure is therefore antiferro-orbitally ordered along $c$ (A-type) and ferro-orbitally ordered in the $ab$ plane. In comparison, in the high temperature cubic phase the $t_{2g}$ orbitals are split into singlet $a_{1g}$ and doublet $e_g$ due to a small trigonal distortion present in the system. The higher energy doublet is equally occupied at each V-site implying the absence of any orbital order unlike the tetragonal phase. Note that the trigonal distortion is also present in the low temperature tetragonal phase alongwith the tetragonal distortion. Here we discuss our results in the $(d_{xy}, d_{yz}, d_{xz})$-basis instead of $a_{1g}$ and $e_g$.

While the A-type orbital ordering observed by Motome and Tsunetsugu for ZnV$_2$O$_4$ with alternately occupied $d_{xz}$ and $d_{yz}$ orbital along the $c$-direction (Fig. 1 right panel) is found to be inconsistent with the underlying space group symmetry of the crystal (I4$_1$/amd), the orbital order described in the present work is compatible with the crystal symmetry as it is obtained from a self-consistent field calculation on the crystal structure described by the I4$_1$/amd spatial group (Fig. 1 left panel).

The orbital order described above is driven by the combination of the staggered distortion present in the experimental lattice structure with correlation effects. First of all, the cubic to tetragonal transition with a compression of the VO$_6$ octahedron along the $c$-axis splits the triply degenerate $t_{2g}$ states into a lower energy $d_{xy}$-orbital and higher energy doublet which are linear combinations of $d_{xz}$ and $d_{yz}$ orbitals (i.e. $d_{xz} \pm d_{yz}$), then the degeneracy in the higher energy doublet is lifted at each vanadium site due to a co-operative Jahn-Teller (JT)-like distortion (combination of trigonal distortion of the V sites) present in the experimental lattice structure which makes the O-V-O angles to alternate between 85° and 95° in a staggered fashion along $c$-axis. Hence the faces of $V_4O_4$ cubes in the $ab$-plane alternately expand or compress along the $c$-axis (see Fig. 4). LDA calculations, due to its known inabilities to describe this type of electronically driven cooperative JT distortion, fail to lift the degeneracy of the higher energy doublet and both $d_{xz} \pm d_{yz}$ orbitals are partially filled at each V-site. Consideration of $U$ completely lifts this degeneracy and an orbital ordering is obtained as shown in Fig. 4.

In the next step of our calculations we perform a relativistic calculation including the spin-orbit interaction (LSDA+U+SO) in the second variational method. The magnetization direction is set along the $c$-axis as the experimentally observed spontaneous magnetic moment points to this direction and also this is the high symmetry direction of the tetragonal crystal structure. Within the LSDA+U+SO approach a uniform orbital order (see Fig. 5) is favoured in contrast to the staggered A-type order found within the LSDA+U only approach. The orbital state at each site results from the mixture of the $d_{xz} + id_{yz}$

![FIG. 3: Projected V $t_{2g}$ DOS in the spin up channel within the LSDA+U approach.](Image)

![FIG. 4: (Color online) Three dimensional electron density plots showing the staggered orbital order in this system. The inset shows the occupation of vanadium $t_{2g}$ orbitals in an elementary V$_4$O$_4$ cube. The isovalue used here is 0.6e/A$^3$.](Image)

![FIG. 5: (Color online) Three dimensional electron density plots showing the uniform orbital order within LSDA+U+SO.](Image)
and \(d_{xz} - id_{yz}\) orbitals that were found to be staggered at alternate sites within the LSDA+U. Due to the partial occupation of both \(d_{xz} + id_{yz}\) and \(d_{xz} - id_{yz}\) orbitals, the system has a finite \(l_z = 0.75\) \(\mu_B\) moment. Since this orbital magnetic moment is antiferromagnetically coupled to the spin only magnetic moment (1.69 \(\mu_B\)) we obtain a total magnetic moment of 0.94\(\mu_B\) per vanadium ion. We note that the good agreement with the experimentally observed magnetic moment (0.63 \(\mu_B\)) implies an important contribution of the orbital degrees of freedom in the present system. In fact, LSDA+SO only calculation provides a small orbital moment of about 0.04 \(\mu_B\) due to the inability of LSDA to treat orbital polarization effects\(^{28}\). Including atomic orbital correlations on top of LSDA+SO scheme through the Hubbard \(U\) allows for an appropriate description of the atomic orbital state.

In order to understand the effects of the spin-orbit coupling, we compare in Fig. 6 the bandstructure within LSDA+U (left panel) and LSDA+U+SO (right panel). The bands are shown along the path \(Z(0,0,0) - G(0,0,0) - X(\pi/a,\pi/a,0) - N(\pi/a,0,\pi/c) - Z\). Note the narrowing of the broad \(V\) \(d\) unoccupied band (energy between 0.4 eV and 1.8 eV) when considering SO.

FIG. 6: Bandstructure in the energy interval \((-3,3)\) eV within LSDA+U (spin up channel) (left) and LSDA+U+SO (right). The bands are shown along the path \(Z(0,0,0) - G(0,0,0) - X(\pi/a,\pi/a,0) - N(\pi/a,0,\pi/c) - Z\). Note the narrowing of the broad \(V\) \(d\) unoccupied band (energy between 0.4 eV and 1.8 eV) when considering SO.

and concerning the bandgap because the bandgap is formed in this channel. We compare in Fig. 6 the bandstructure within LSDA+U+SO (right panel). The bands are shown along the path \(Z(0,0,0) - G(0,0,0) - X(\pi/a,\pi/a,0) - N(\pi/a,0,\pi/c) - Z\). Note the narrowing of the broad \(V\) \(d\) unoccupied band (energy between 0.4 eV and 1.8 eV) when considering SO.

An experimental measurement of the band gap in this system could further establish the role of spin-orbit interaction and atomic orbital correlation and thereby corroborate the type of orbital ordering. Our calculations show that this (uniform) orbital ordering persists in the antiferromagnetic phase observed in INS\(^{10,11}\).

In summary, we have investigated the orbital order in 3\(d^2\) magnetically frustrated systems by performing \textit{ab initio} DFT calculations on \(\text{ZnV}_2\text{O}_4\) and observe that although strong onsite electronic correlation effects in the presence of co-operative JT distortion stabilize an \(A\)-type staggered orbital order, the consideration of relativistic spin-orbit effects unquenches the orbital moment and leads to a uniform orbital order state with a large orbital moment. This orbital moment couples antiferromagnetically to the spin moment of \(V\) with a net magnetic moment close to the experimentally observed one. This study shows that for a realistic description of the orbital order in \(\text{ZnV}_2\text{O}_4\) it is the interplay between electron correlation, spin-orbit coupling and co-operative JT distortions what drives the orbital order. Our results help to resolve the differences among all the previous theories and present a consensus picture of the orbital order in \(\text{ZnV}_2\text{O}_4\) compatible with the experimental findings. Furthermore, this work shows direct evidence from \textit{ab initio} calculations of the importance of spin-orbit effects in 3\(d^2\) systems.

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