Orbital Order in ZnV_2O_4

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In view of recent controversy regarding the orbital order in the frustrated spinel ZnV_2O_4, we analyze the orbital and magnetic ground state of this system within an *ab initio* density functional theory approach. While local density approximation + Hubbard U calculations in the presence of a cooperative Jahn-Teller distortion stabilize an A-type staggered orbital order, the consideration of relativistic spin-orbit (SO) 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 *ab initio* calculations are able to resolve the existing discrepancies in previous theories and that it is the SO 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 center stage of condensed matter physics research for the last three decades because of their intriguing, often nonintuitive 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 [1,2]. Besides being of fundamental interest, spinels have been also proposed for spintronics applications [3]. In the present work on ZnV_2O_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 ZnV_2O_4 as well as in other vanadium spinels such as MgV_2O_4 and CdV_2O_4 is presently a subject of considerable debate [4]. In order to understand the behavior of these compounds, various groups [5–7] 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 V^{3+} ions in a spin 1 state characterized by double occupancy of the triply degenerate t_{2g} 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 [8]. In ZnV_2O_4 the interplay of all these degrees of freedom leads to two successive phase transitions involving structural, orbital, and magnetic changes. At $T_S = 51$ K, ZnV_2O_4 undergoes a structural phase transition where the symmetry is lowered from cubic to tetragonal with a compression of the VO_6 octahedron along the c axis [9] and the system possibly orbital orders. This also lifts the geometrical frustration of the cubic phase making way for the second transition at $T_N = 40$ K which is of a magnetic nature and the system orders antiferromagnetically [9,10].

While the antiferromagnetic structure in ZnV_2O_4 at $T < T_N$ has been unambiguously determined by neutron scattering experiments at low temperatures [11], the nature of the orbital ground state in the whole temperature range $T < T_S$ is still unclear. Tsunetsugu and Motome [5] 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 ground state 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). Although this orbital order is shown to be consistent with low temperature antiferromagnetic order as well as with the compressed VO_6 octahedron, it breaks the mirror and glide symmetries along (110), (1$\bar{1}$0) and (110), (1$\bar{1}$0) planes, respectively. Hence it is found to be inconsistent with the spatial symmetry $I4_1/amd$ predicted by x-ray scattering experiments on polycrystalline samples [9,12]. Recent inelastic neutron scattering data on a single crystal sample [2] seem to suggest though a breaking of the glide symmetry. These results have nevertheless not been further corroborated.

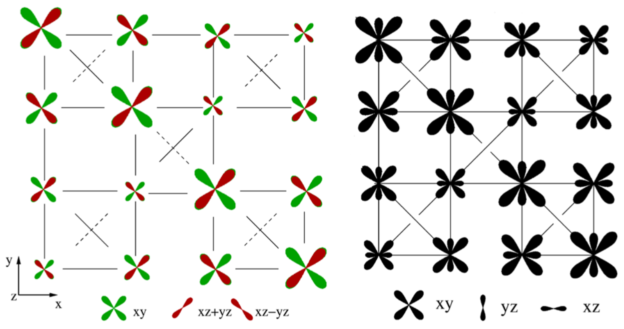

FIG. 1 (color online). Schematic diagram showing the orbital order obtained within LDA + U in this work (left panel) and that proposed in Ref. [5] (right panel).

Tchernychyov [6], in a separate theoretical work, considering the fact that V^{3+} has a non-negligible orbital moment, proposed a single-ion model where the relativistic SO 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 $d_{xz} \pm id_{yz}$ at each V site. This orbital order is consistent with the symmetry $I4_1/amd$ since it preserves both mirror and glide symmetries and hence is at odds with the prediction of Tsunetsugu *et al.* [5]. Di Matteo *et al.* [7] proposed a third alternative model where both the relativistic SO coupling and the Kugel-Khomskii model of spin-orbital superexchange are treated on an equal footing and observed that for intermediate SO coupling strength the ground state of the system shows a uniform orbital order compatible with Tchernychyov's prediction and $I4_1/amd$ symmetry.

In view of the above mentioned disagreements among the various theoretical models, we analyze in this work the orbital and magnetic ground state of ZnV_2O_4 in the tetragonal phase within an *ab initio* density functional theory (DFT) approach. Our calculations without SO 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 [5] about the existence of a staggered orbital order except that we obtain a pattern which, contrary to Ref. [5], is compatible with the underlying $I4_1/amd$ symmetry (see Fig. 1). Inclusion of relativistic SO effects in our DFT calculations changes the picture considerably. For moderate to large values of the on-site electronic correlation U, a uniform orbital order analogous to the cubic phase [13]—where the orbitals are tilted due to the trigonal distortion of the structure—is stabilized. Also, a large orbital moment antiparallel to the spin moment is obtained in the presence of strong on-site 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 [9,10] minimizes the *ab initio* DFT calculations.

Our DFT calculations were performed within the local spin density approximation (LSDA) and the LSDA + U [14] approach. The SO coupling was treated using a scalar-relativistic basis and the second variational method [15] (LSDA + U + SO). All calculations were done with the full-potential linearized augmented plane-wave code WIEN2K [16]. 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 **k** points mesh in the irreducible wedge was considered for Brillouin zone integrations. Structural data were taken from Ref. [9].

In Fig. 2(a) we present the spin polarized density of states (DOS) of Zn, V, and O within LSDA The V t_{2g} up spin states are partially occupied defining a metallic solution within 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. Because of 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).

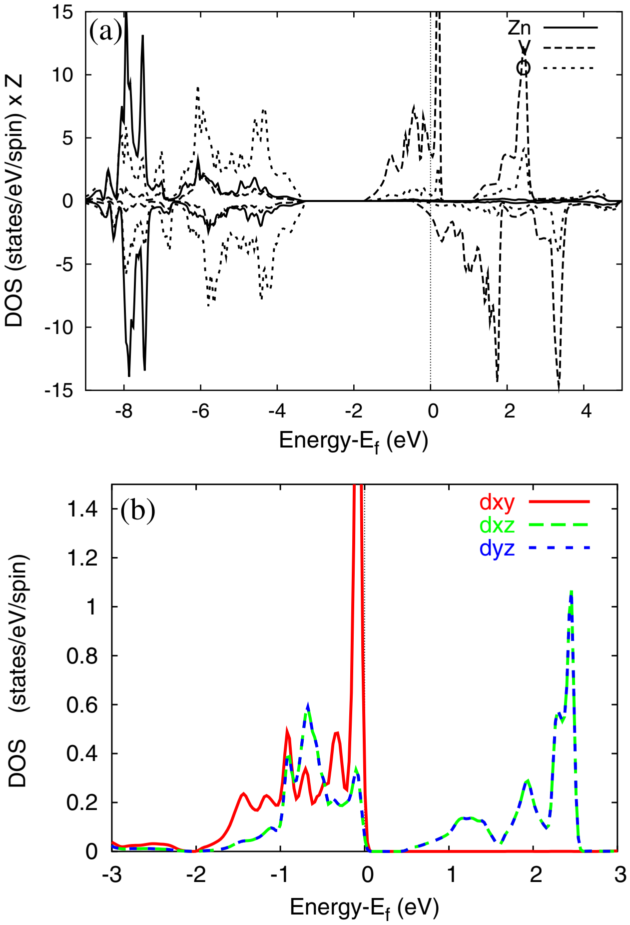

FIG. 2 (color online). (a) Total DOS for Zn, V, and O in both spin up and down channel in LSDA. (b) Projected V t_{2g} DOS in the spin up channel within the LSDA + U approach.

ZnV_2O_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 [17] 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. 2(b) 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 [18]. 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. The orbital ground state described below is found to be stable with U values in the range 4–6 eV.

We present in Fig. 3 a three-dimensional plot of the spin density of ZnV_2O_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. 3 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_b bonds and c axis directed along the apical V-O_a bond). This feature is already observed in the projected DOS in Fig. 2(b). 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. 3). The V_4O_4 cube [Fig. 3 (inset)] shows 2 V with the second t_{2g} electron in a $d_{xz} + d_{yz}$ symmetry and 2 V with the second t_{2g} electron in a $d_{xz} - d_{yz}$ symmetry.

This orbital structure is therefore antiferro-orbitally ordered along c and ferro-orbitally ordered in the ab plane (A type). 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. 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 along with 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 [5] for ZnV_2O_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 cooperative 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 the c axis. Hence the faces of V_4O_4 cubes in the ab plane alternately expand or compress along the c axis (see Fig. 3). LDA calculations, due to its known inabilities to describe this type of electronically driven cooperative JT distortion [17] 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. 3.

In the next step of our calculations we perform a relativistic calculation including the SO 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. 4) is favored 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 $d_{xz} + id_{yz}$ and $d_{xz} - id_{yz}$ orbitals that were found to be staggered at alternate sites within the LSDA + U. Because of the partial occupation of both $d_{xz} + id_{yz}$ and $d_{xz} - id_{yz}$ orbitals, the system has a

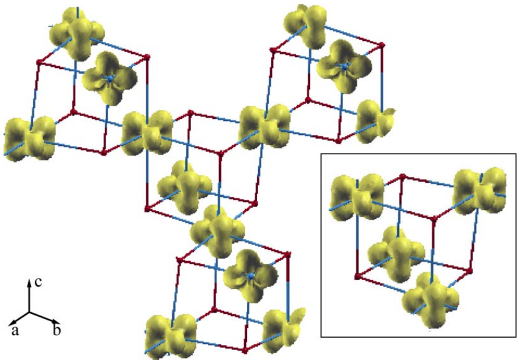

FIG. 3 (color online). Three dimensional electron density plots showing the staggered orbital order in this system [an elementary V_4O_4 cube in inset (see text)].

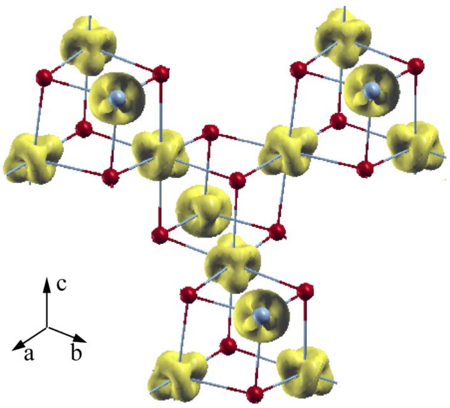

FIG. 4 (color online). Three dimensional electron density plots showing the uniform orbital order within LSDA + U + SO.

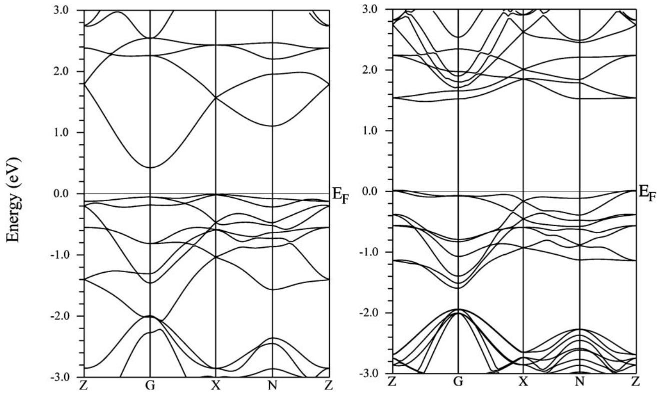

FIG. 5. Band structure within LSDA + U (spin up channel) (left) and LSDA + U + SO (right) along the path $Z(0, 0, 2\pi/c) - G(0, 0, 0) - X(\pi/a, \pi/a, 0) - N(\pi/a, 0, \pi/c) - Z$.

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 ($0.63\mu_B$) [9] 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 [19]. Including atomic orbital correlations on top of the 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 SO coupling, we compare in Fig. 5 the band structure within LSDA + U (left panel) and LSDA + U + SO (right panel). In the LSDA + U case, the spin-up bands are shown because the band gap is formed in this channel, whereas the spin down bands are about 1 eV above the Fermi level. The significant increase in the band gap within the LSDA + U + SO approach (1.0 eV) can be understood by the fact that the small but finite orbital moment ($\sim 0.04\mu_B$) obtained within LSDA + SO is driven to about $0.75\mu_B$ by the orbital polarization effects of U. With this large orbital moment, the SO interaction term in the Hamiltonian pushes the unoccupied d bands above the Fermi level further up in energy. We also observe a decrease in the bandwidth of these bands compared to the case of LSDA + U and thereby a substantial increase in the band gap.

An experimental measurement of the band gap in this system could further establish the role of SO 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 [9,10].

In summary, we have investigated the orbital order in $3d^2$ magnetically frustrated systems by performing *ab initio* DFT calculations on ZnV_2O_4 and observe that although strong onsite electronic correlation effects in the presence of cooperative JT distortion stabilize an A-type staggered orbital order, the consideration of relativistic SO 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 ZnV_2O_4 it is the interplay between electron correlation, SO coupling, and cooperative JT distortions that 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 ZnV_2O_4 compatible with experimental findings. Furthermore, this work shows direct evidence from *ab initio* calculations of the importance of spin-orbit effects in $3d^2$ systems.

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