Proposed Orbital Ordering in MnV$_2$O$_4$ from First-principles Calculations

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(Dated: May 22, 2009)

Based on density functional calculations, we propose a possible orbital ordering in MnV$_2$O$_4$ which consists of orbital chains running along crystallographic $a$ and $b$ directions with orbitals rotated alternatively by about 45$^\circ$ within each chain. We show that the consideration of correlation effects as implemented in the local spin density approximation (LSDA)+U approach is crucial for a correct description of the space group symmetry. This implies that the correlation-driven orbital ordering has a strong influence on the structural transitions in this system. Inclusion of spin-orbit effects does not seem to influence the orbital ordering pattern. We further find that the proposed orbital arrangement favors a noncollinear magnetic ordering of V spins, as observed experimentally. Exchange couplings among V spins are also calculated and discussed.

PACS numbers: 71.20.-b,71.15.Mb, 71.70.Ej, 75.10.-b

The spinel compounds with a chemical formula of AB$_2$X$_4$ where B sites are usually transition metal ions, form a frustrated pyrochlore lattice with corner-sharing tetrahedra. These compounds show a complex behavior including structural transitions from cubic to tetragonal symmetries which are often accompanied by an orbital order–disorder transition as well as complicated magnetic orderings at low temperatures.

The spinel MnV$_2$O$_4$ has experienced a recent surge in activities due to new experimental observations in single crystals revealing a lower symmetry structure than previously suggested. This has important implications for the related orbital order at low temperatures which is still unclear. The presence of two magnetic ions in MnV$_2$O$_4$ (Mn with spin 5/2 and V with spin 1) translates into more complex magnetic phase transitions in this system than in other vanadium spinel oxides such as ZnV$_2$O$_4$, MgV$_2$O$_4$ or CdV$_2$O$_4$ with nonmagnetic A-site ions. Recent experimental findings indicated that MnV$_2$O$_4$ undergoes a phase transition from paramagnetic to a collinear ferrimagnetic phase at 56K where the Mn and V spin moments point in opposite directions. At $T = 53K$ a second magnetic phase transition to noncollinear ferrimagnetism follows accompanied by a structural transition from cubic to tetragonal phase.

The cubic to tetragonal structural transition in MnV$_2$O$_4$ is, similar to other vanadium spinels, associated with a compression of the VO$_6$ octahedron ($c_T/a_T = 0.98$). The octahedral environment of V (VO$_6$) splits the d states into lower t$_{2g}$ and higher e$_g$. Since V$^{+3}$ is in a 3d$^2$ configuration, the t$_{2g}$ orbitals are partially filled and possible orbital orderings may occur. Earlier experimental observations indicated the tetragonal space group to be I4$_1$/amd. However, recent precise measurements on a single crystal showed that the tetragonal space group is I4$_1$/a. Since the orbital order and, accordingly, the magnetic order are closely related to the underlying space group symmetry, it is very important to establish the space group symmetry unambiguously.

The I4$_1$/a space group breaks the mirror and glide symmetries present in the I4$_1$/amd space group, which implies that two of the four V-O bonds in the ab plane are shorter whereas in I4$_1$/amd symmetry all four V-O bond lengths are the same. Garlea et al. proposed a staggered A-type orbital ordering for this system based on their observations of the structural and magnetic phases at low temperature. A similar ordering was also proposed by Suzuki et al. Though the magnetic structure at low temperatures has been unambiguously established by the above mentioned experiments, there has not yet been any experiment such as X-ray resonant spectroscopy to directly probe the orbital order. Determination of exchange couplings using neutron scattering techniques by Chung et al. is in apparent contradiction with the proposed staggered A-type orbital ordering. As pointed out by these authors, the proposed orbital order in Refs. 2,4 lacks the consideration of trigonal distortion, which is found to be strongest in MnV$_2$O$_4$ among all the vanadium spinel. The trigonal distortion has often shown to have significant effects on the orbital order.

In this Letter we show, based on density functional theory (DFT) calculations, that the ground state tetragonal space group symmetry at low temperatures is I4$_1$/a and strongly driven by correlation effects. We propose an orbital ordering consisting of orbital chains running along the axes $a$ and $b$ with orbitals rotated by about 45$^\circ$ within each chain. This ordering favors a noncollinear arrangement of spins, as observed experimentally, which is a convincing indication of its existence.

For our DFT calculations we considered a combination of three different methods, namely: (a) plane wave-based method (b) linear augmented plane wave (LAPW) method and (c) muffin-tin orbital (MTO) based N-th order MTO (NMTO) method. Results were cross-checked among the three schemes in terms of total energy differences, density of states and band structures. Since first principles calculations take into account all structural and chemical aspects appropriately, we expect to
We first performed a structural optimization using the plane wave method as implemented in the Vienna Ab-initio Simulation Package (VASP) and considered exchange-correlation functionals within LSDA, generalized gradient approximation (GGA) and LSDA+U in order to investigate the relative stability between \(I4_1/amd\) and \(I4_1/a\) symmetries in MnV\(_2\)O\(_4\). We used projector augmented wave (PAW) potentials in the LSDA+U approach, with different choices of U values (\(U=4.5\) eV) and consideration of correlation effects in the V \(d\)-orbitals. The charge densities and potentials were represented by spherical harmonics up to \(l=6\). For Brillouin- zone (BZ) integrations we considered a 52\(\times\)6\(\times\)6\(\times\)6 mesh in the irreducible wedge and the modified tetrahedron method was applied. The collinear ferrimagnetic spin arrangements between Mn and V was taken the same as for the structural optimization calculations. In all further calculations we considered the LSDA+U approximation and fixed the value of U at 4.5 eV which reproduces the experimentally observed orbital moment in vanadium, as will be discussed later.

In Fig. 1 we show the electronic density of states (DOS) calculated within the LSDA+U approximation. In the partial DOS one observes the usual \(t_{2g}\) (consisting of \(x^2-y^2\), \(xz\) and \(yz\) orbitals defined in the crystallographic coordinate system) and \(e_g\) (consisting of \(xy, 3z^2\)) splitting of \(V d\)-orbitals due to the O octahedral crystal field. Inclusion of correlation effects in the \(V d\)-orbitals through the LSDA+U approach, splits the \(t_{2g}\) states further and opens a gap of 1.1 eV. The degeneracy between all the three \(t_{2g}\) orbitals is lifted in the low symmetry \(I4_1/a\) group. All \(t_{2g}\) orbitals are partially occupied with higher \(x^2-y^2\) and \(yz\) occupancy compared to \(xz\). This becomes more evident in the band structure results. Fig. 2 shows the \(t_{2g}\) bandstructure in the majority spin channel, which is separated from occupied O-\(p\) dominated bands by a gap of 1.5 eV and from unoccupied \(e_g\)-like bands by a gap of 0.2 eV. The flatness of the bands indicates the projected band characters of \(x^2-y^2\), \(xz\) and \(yz\) orbitals.

**TABLE I:** Energy-minimized structural parameters for MnV\(_2\)O\(_4\). Lattice constants were kept at the experimental values. The LSDA+U optimized structural parameters show the \(O\) \(x\)-coordinate to be non-zero, signaling the change of space group symmetry to \(I4_1/a\).

|      | LSDA | GGA | LSDA+U (\(U=4.5\) eV) |
|------|------|-----|------------------------|
| Mn   | 0.0 0.25 0.125 | 0.0 0.25 0.125 | 0.0 0.25 0.125 |
| V    | 0.0 0.0 0.5   | 0.0 0.0 0.5   | 0.0 0.0 0.5 |
| O    | 0.0 0.0243 0.7392 | 0.0 0.0236 0.7394 | 0.0059 0.0244 0.7383 |
Significant mixing of orbitals happens due to the low symmetry of the $I4_1/a$ space group. In Fig. 3 we show the three-dimensional electron density of occupied V $t_{2g}$ orbitals on a real space grid. We identify a long range order pattern for the orbital distribution. Contrary to the proposed staggered A-type order \cite{4}, we do not observe any significant difference in charge density, from that of LSDA+U. The value of the orbital moment depends sensitively on U. The experimental V moment is best described for $U=4.5$ eV. At this U value we obtain an orbital moment of about 0.34 $\mu_B$ at V site which is antiparallel to the spin-moment ($1.65\mu_B$). The total magnetic moment of 1.31 $\mu_B$ is close to the measured value of 1.3 $\mu_B$. Also, the calculated magnetic moment at the Mn site is found to be 4.24 $\mu_B$ in good agreement with the experimental estimate. The orbital moment at the V site seems to develop an appreciable value only beyond a critical U value, $U_c$ ($3.0$ eV $< U_c < 4.5$ eV) \cite{22}, which may be interpreted as Coulomb enhanced spin-orbit effect \cite{22}.

We note that the perfect antiferro-orbital ordering as proposed by Refs. \cite{4} and \cite{2} would imply a quenching of orbital moment. The presence of a finite orbital moment can be associated with the breakdown of perfect antiferro-orbital ordering and may explain the domain alignment by magnetic field as observed by Ref. \cite{4}.

We have also computed the magnetic exchange couplings from first principles by considering LSDA+U total energy calculations with the PAW basis for different spin alignments of V atoms within the V tetrahedra. Mapping the total energies to a Heisenberg like model, we obtain exchange interactions along the orbital chains (J) of 11 meV and between the chains (J') of 2 meV. This implies $\alpha = J'/J \approx 0.2$ compared to 0.3 found by Chung et al.\cite{22}. Perfect antiferro-orbital ordering with xz and yz alternately occupied along the c-axis would however yield much smaller ratios of $J'/J$, since the overlap between orthogonal yz and xz orbitals at neighboring sites would have been nearly zero. The moderately strong value of J', as obtained in the DFT calculation, originates from large mixing of different $t_{2g}$ orbitals influencing the overlap of the renormalized orbitals at neighboring sites.

Our calculations described so far assume the collinear arrangement of V spins, while experiment reports a transition from collinear to noncollinear spin arrangements coincident with the structural phase transition. In order to check whether our proposed orbital order sustains
a noncollinear arrangement of V spins, we performed PAW calculations where we relaxed the V spin orientation keeping the Mn spins aligned parallel to the c axis. The relaxed spin structure shows the V spins to be canted with respect to the c axis by about 63°, which is in very good agreement with the experimentally estimated canting of 65.5°. The noncollinear spin arrangement was found to be slightly favoured over the collinear ferrimagnetic spin arrangement by an energy gain of 3 meV. Though this energy difference is almost within the accuracy limit of DFT, the good agreement between theory and experimental estimates is encouraging.

To conclude, we have carried out DFT-based first-principles calculations to investigate the nature of the orbital ordering in MnV$_2$O$_4$ which is closely associated with the transition from a high temperature cubic structure to a low temperature tetragonal structure. Our geometry-optimized structures for MnV$_2$O$_4$ show a strong influence of correlation effects in the choice of the correct low temperature structure. The obtained ground state structure, $I4_1/a$ looses the mirror and glide symmetry compared to the alternative proposed candidate $I4_1/amd$. The O in $I4_1/a$ are in 16f positions with nonzero x-coordinate, which makes the V-O bondlengths even in the ab-plane to be unequal. This lowering of symmetry necessarily breaks the degeneracy of the t$_{2g}$ states completely and also introduces mixing between different t$_{2g}$ states. The resulting eigenstates therefore turn out to be of mixed-character and nondegenerate, which get filled up by two V electrons. The occupied orbitals follow the site symmetry of vanadium which is 4-fold rotation times inversion to give rise to orbital chains with orbitals rotated with respect to each other both within and between the chains. Our DFT computed V-V magnetic coupling is found to be in agreement with the experimental findings. These results provide an explanation of the controversy between antiferro-orbital ordering versus the strong exchange between orbital chains ($J'$). We further showed that our proposed orbital ordering is capable of predicting correctly the noncollinear spin structure as observed experimentally. Further experiments like X-ray resonant spectroscopy would be helpful to probe directly our proposed orbital order.

Acknowledgements- We acknowledge useful discussions with J. Gl"ummenn and D. Khomskii. TSD thanks Swarnajayanti Grant and MPI, Stuttgart through partner-group program. RV thanks the DFG for financial support through the SFB/TRR49 program. SS thanks CSIR for financial support.

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