Effect of spin–orbit coupling on magnetic and orbital order in MgV$_2$O$_4$

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Abstract

Recent measurements on MgV$_2$O$_4$ single crystals have reignited the debate on the role of spin–orbit (SO) coupling in dictating the orbital order in vanadium spinel systems. Density functional theory calculations were performed using the full-potential linearized augmented-plane-wave method within the local spin density approximation (LSDA), Coulomb correlated LSDA (i.e. LSDA + $U$), and with SO interaction (LSDA + $U$ + SO) to study the magnetic and orbital ordering in the low temperature phase of MgV$_2$O$_4$. It is observed that, in the experimental antiferromagnetic phase, the spin–orbit coupling affects the orbital order differently in alternate V-atom chains along the $c$-axis. This observation is consistent with the experimental prediction that the effect of spin–orbit coupling is intermediate between those in the cases of ZnV$_2$O$_4$ and MnV$_2$O$_4$.

(Some figures may appear in colour only in the online journal)

1. Introduction

Vanadium spinels AV$_2$O$_4$ (A = Mg, Zn, Cd) have become the subject of extensive study in recent years [1–6], as they provide a very interesting playground for the study of competing interactions on a frustrated lattice in three dimensions. The vanadium (V) ions at the B sites of the spinel structure form a geometrically frustrated pyrochlore lattice, with corner sharing tetrahedra. In its $3^+$ valence state, the V ion has two electrons in the d shell, which, because of a strong Hund’s coupling, align parallel to each other, thereby imparting a high spin state ($S = 1$) to the ion. Thus, in this family of spinels, there is a magnetic ion on a geometrically frustrated lattice resulting in competing ground states. Things get more involved when the partial occupancy of triply degenerate $t_{2g}$ orbitals by the two d electrons makes the orbital degree of freedom unfrozen. As both spin and orbital degrees of freedom remain active, there is a high possibility of spin–orbit (SO) coupling playing an important role in the low-energy physics of this family of systems. The role of this interaction in these systems has been a matter of debate recently [1, 3, 4]. The manifestation of the interplay of orbital, spin and lattice degrees of freedom in these systems culminates in experiments as a sequence of phase transitions [1, 7, 8]. A structural transition, often followed by a magnetic transition as the temperature is lowered, signifies competing interactions trying to stabilize a particular ground state with gradual lifting of the frustration.

MgV$_2$O$_4$, with a normal spinel structure, has been reported to undergo a structural transition at 51 K from cubic to tetragonal symmetry, and a magnetic transition at 42 K from non-magnetic to an antiferromagnetic (AFM) phase consisting of alternating antiferromagnetic chains of V atoms running parallel to $a$- and $b$-axes as one goes along the $c$-axis [1, 9]. The high temperature (HT) phase has a cubic spinel structure with $F43m$ symmetry, where the V ion is surrounded by an almost perfect O$_6$ octahedron with all six V–O bonds having the same length. This leads to a sizable $t_{2g}$–$e_g$ crystal field splitting (~2.5 eV) of the d levels [1]. There is of course a small trigonal distortion also present in this phase. Experimental results further reveal that the structural transition to the tetragonal phase at 51 K is accompanied by a compression along the $c$-axis with $c/a = 0.9941$. This lowers the symmetry to space group $I4/m2$. Hence, in addition to the $t_{2g}$–$e_g$ splitting arising from roughly O$_6$ octahedral coordination, a further splitting occurs...
due to the tetragonal compression where the low lying \(t_{2g}\) triplet splits into a lower energy singlet (\(d_{xy}\) orbital) and a higher energy doublet of \(d_{yz}\) and \(d_{zx}\) orbitals. Thus orbital degeneracy is partially lifted with this structural distortion. Consequently, out of the two d electrons, one goes to the lower energy \(d_{xy}\) orbital, while the other still has a choice as it occupies the doubly degenerate \(d_{yz}\) and \(d_{zx}\) orbitals. This opens up a possibility of orbital order in this system. Structural transition also partially lifts the frustration of the V–V bonds in the pyrochlore lattice. This culminates in the second transition, at lower temperature of 42 K, where a long range antiferromagnetic order sets in [1]. Thus, in all the vanadium spinels, the presence of orbital order (if any) and the magnetic order observed at low temperatures is interrelated.

Several theoretical models have been proposed in the last few years to explain the possible orbital order in vanadium spinels so as to be consistent with the observed antiferromagnetic order. Among these, the model proposed by Tsunetsugu and Motome [3] (for \(AV_2O_4; A = Zn, Mg, Cd\) is based on the strong coupling Kugel–Khomskii Hamiltonian and predicts an orbital order where, at each V site, the \(d_{xy}\) orbital is occupied by one electron and the second electron occupies either the \(d_{xz}\) or \(d_{yz}\) orbital alternately along the c-axis. However, this type of orbital order was found to be of lower symmetry than that (\(J_{4z}/amal\)) observed experimentally for \(ZnV_2O_4\). In an alternative theoretical model, Tchernychov [4] considered a dominant SO interaction, which then led to the proposal that the second electron would occupy a complex orbital of the type \(d_{xz}\pm id_{yz}\) at each V site. This orbital order is found to be consistent with the underlying crystal symmetry. Also, it explains the low magnetic moment per V ion observed in these systems, since a large negative orbital moment is expected from a strong SO coupling. These findings were also corroborated by electronic structure calculations [5] for \(ZnV_2O_4\).

However, recent measurements on other members of the vanadium spinel family raise doubts about the presence of a strong spin–orbit interaction effect. In fact, there has been a tremendous effort, from both theoreticians and experimentalists working on these systems, to bring out a unified picture in terms of the important interactions which underlie the two phase transitions (one structural and the other magnetic). In \(ZnV_2O_4\), the SO coupling is found to be significant both theoretically and experimentally [4, 5, 10], whereas in the case of \(MnV_2O_4\) there seems to be very little or no effect of the SO interaction on the orbital order [11, 12]. Recently, Wheeler et al [11] performed neutron diffraction measurements on an \(MgV_2O_4\) single crystal and speculated on the basis of their observations that \(MgV_2O_4\) might fall in between \(ZnV_2O_4\) and \(MnV_2O_4\) as far as the strength of the SO coupling is concerned. Hence it is expected that in \(MgV_2O_4\) the occupied orbitals at V sites, instead of being real at all V sites (Tsunetsugu and Motome model) or complex at all V sites (Tchernychov model), could be real at some V sites and complex at others. In a previous theoretical study on \(MgV_2O_4\) [13], the issue of the impact of SO coupling on orbital order was not investigated, whereas, as stated above, experimental observations indicate that the SO coupling in \(MgV_2O_4\) is likely to be non-negligible. In order to investigate thoroughly the effect of SO interaction on magnetic and orbital order in \(MgV_2O_4\), we have carried out first principle electronic structure calculations incorporating SO coupling. Such a calculation is definitely expected to unfold the strength of SO coupling in this system, and also the nature of orbital order (if there is any) and correlation of experimentally observed magnetic order with the orbital order, if present.

2. Methodology

We undertake an electronic structure calculation using the full-potential linearized augmented plane-wave method with the basis chosen to be linearized augmented plane waves as implemented in the WIEN2K code [14]. The calculations have been carried out with no shape approximation to the potential and charge density. These calculations were performed at three levels of sophistication: using the local density approximation (LSDA), the Coulomb correlated LSDA + \(U\) approximation, and next with SO interaction, i.e. LSDA + \(U\) + SO approximation. To remove the self-Coulomb and self-exchange–correlation energy included in the LSDA approximation, we use a self-interaction corrected scheme (LSDA + \(U\) (SIC)) [15], which is appropriate for the strongly correlated systems. The corrected energy functional is written as [15]

\[
E = E^{\text{LSDA}} - \frac{1}{2} (U_{mm'}\delta_{\sigma\sigma'} - \sum_{n, m''} J_{nn''}(\delta_{\sigma\sigma'} - \delta_{\sigma'\sigma})) + \frac{1}{2} \sum_{m, m', \sigma} (U_{mm'} - J_{mm'})\delta_{\sigma\sigma'} \delta_{\sigma'\sigma}.
\]

Here \(E^{\text{LSDA}}\) is the standard LSDA energy functional, \(U\) represents the on-site Coulomb interaction, \(J\) is the exchange parameter and \(n_{\sigma\sigma'}\) are the occupations of the localized orbitals. \(N\) is the total number of localized electrons.

In the LSDA + \(U\) + SO calculations, SO coupling was considered within the scalar relativistic approximation and the second variational method was employed [16]. In this method, the eigenvalue problem is first solved separately for spin-up and spin-down states without inclusion of the SO interaction term (\(H_{SO}\)) in the total Hamiltonian. The resulting eigenvalues and eigenfunctions are then used to solve a new eigenvalue problem with the \(H_{SO}\) term in the total Hamiltonian. The resulting eigenvalues and eigenfunctions are then used to solve a new eigenvalue problem with the \(H_{SO}\) term in the total Hamiltonian. This method is more efficient and computationally less expensive than the calculation in which \(H_{SO}\) is included in the total Hamiltonian by doubling the dimension of the original eigenvalue problem in order to calculate the non-zero matrix elements between spin-up and spin-down states. In this method, the calculation of \(H_{SO}\) matrix elements involves a much smaller number of basis functions than in the original basis set.

\(MgV_2O_4\) crystallizes in tetragonal structure with symmetry \(\bar{4}m2\) (space group 119) at low temperatures [1]. Atomic positions and lattice constants were taken from the experimental data [1]. The atomic sphere radii were chosen to
Figure 1. Corner sharing network of $V_4O_4$ cubes in the low temperature structure of Mg$V_2O_4$ showing the experimentally observed magnetic order. The solid and dotted lines joining the V atoms (shown in one cube) represent the shorter V–V FM bonds (2.971 Å) and longer V–V AFM bonds (2.98 Å), respectively. The inset shows VO$_6$ octahedra for two inequivalent vanadium sites with four different types of V–O bond observed in Mg$V_2O_4$ and their orientations.

Table 1. Total-energy difference (meV) per formula unit between the FM, AFM$_A$ and AFM$_B$ phases and band gap $E_g$ in AFM phase under various approaches.

| Method        | $\Delta E_1$ | $\Delta E_2$ | $E_g$ (eV) |
|---------------|--------------|--------------|------------|
| LSDA          | 145.26       | 65.9         | —          |
| LSDA + $U$   | 82.62        | 48.47        | 0.12       |
| LSDA + $U + SO$ | 107.89      | 103.13       | 0.34       |

We have used 50 k-points in the irreducible part of the Brillouin zone for the self-consistent calculations. In order to model the low temperature magnetic order observed in the experiment, we have constructed a supercell (with eight inequivalent vanadium atoms). The lowering of symmetry of this unit cell arises due to the experimentally observed antiferromagnetic ordering. The network of corner sharing $V_4O_4$ cubes of low temperature structure is shown in figure 1 with the magnetic order. The eight inequivalent vanadium atoms with the corresponding orientation of spins considered in this calculation are marked in the figure. One can see the antiferromagnetic chains along $a$ (V3–V7–V3–V7) and $b$ (V6–V2–V6–V2) axes alternating along the c-axis. In each $V_4O_4$ cube there are four inequivalent V atoms. Due to the presence of cooperative trigonal distortion along the c-axis resulting in alternating compression and expansion of cube faces, there is a further symmetry breaking and hence successive cubes along the c-axis no longer remain equivalent. Furthermore, the $V_4O_4$ cube containing V1, V5, V2 and V6 does not have the same spin arrangement as that containing V3, V7, V4 and V8. Therefore, to model the experimentally observed magnetic order one needs to consider eight inequivalent V atoms in the unit cell.

Figure 2. Spin polarized (a) total DOS for Mg, V and O within LSDA, (b) partial DOS for V d states around the Fermi level within LSDA + $U$, (c) partial d-DOS within LSDA + $U + SO$ ($U − J = 2$ eV) in the low temperature AFM phase.

3. Results

Our LSDA calculations of the experimentally observed AFM phase show that the total energy of this phase is indeed lower than that of the ferromagnetic (FM) phase by 0.145 eV per formula unit (table 1). The density of states (DOS) of the energetically favored AFM phase (within the LSDA) is shown in figure 2(a). Mainly V d states are seen to be present around the Fermi level. We find that LSDA gives a metallic state whereas the system is known to be a Mott
insulator [17]. Thus AFM interaction alone is not able to open up the gap. In an effort to have an insulating behavior consistent with experimental observations, we included Coulomb correlation in our calculations to work within the LSDA + $U$ approximation. We performed calculations with $U_{\text{eff}} = (U - J)$ values in the range 1–4 eV, found to be relevant from the literature on vanadium spinel systems [5, 11, 13]. The results have been presented for $U_{\text{eff}} = 2$ eV in the following; nevertheless, it may be noted that our conclusions remain valid in the mentioned range of $U_{\text{eff}}$ values. We also optimized the oxygen positions keeping the lattice parameters at their experimental values. We observed that the optimized V–O bond lengths are quite close to the experimental ones shown in the inset of figure 1. Table 1 compares the total energies of ferromagnetic, experimentally observed AFM phase and another hypothetical AFM$_0$ phase studied by us (which has ferromagnetic vanadium chains aligned antiferromagnetically along the c-axis). It clearly shows that the AFM phase remains consistently the lowest energy state within all three approximations (results with LSDA + $U$ + SO approximation discussed later) that we have applied in the study. The atomic relaxation under various approximations considered here does not change the trend of total energies. Hence in the following we present the results for the AFM phase in detail. Table 1 also lists the energy band gaps obtained within the LSDA + $U$ and LSDA + $U$ + SO approximations of the AFM phase. We find that the band gap increases when both Coulomb correlation and the spin–orbit interaction are taken into account, as also observed in other vanadium spinels [5]. It may be noted that the density functional theory calculations are known to underestimate the band gaps (often quite substantially, as reported for some other vanadium systems [18]). Hence the band gap values reported here effectively show a qualitative trend within various approximations used.

In figure 2(b) we show the partial DOS of the five d-orbitals, these being the states present around the Fermi level. As expected, the application of Coulomb correlation $U$ is able to open up a small gap of 0.12 eV, which increases with the increase in $U$. The gap originates because of the splitting of the $t_{2g}$ levels in addition to the $t_{2g}$–$e_g$ splitting due to octahedral field. The splitting of $t_{2g}$ (i.e. the gap) is primarily caused by the antiferromagnetic interaction and becomes larger in the presence of Coulomb correlations. Another observation that can be clearly made from the partial DOS of the d orbitals (figure 2(b)) is that, among the occupied $t_{2g}$ orbitals, one orbital (i.e. $d_{xz}$) is more populated, while the other two ($d_{xy}$ and $d_{yz}$) essentially have the same occupancy and seem to be degenerate. The higher occupancy of the $d_{xz}$ orbital is a result of the presence of tetragonal compression along the c-axis at low temperatures. However, closer analysis of the occupancies of the apparently degenerate $d_{xz}$ and $d_{yz}$ orbitals at each vanadium site shows that there is a tendency towards orbital ordering. Table 2 lists the orbital occupancies of $d_{x^2-y^2}$, $d_{xz}$ and $d_{yz}$ for the eight inequivalent V atoms for the experimentally observed AFM order and also for complete FM ordering of vanadium spins. One clearly observes that the occupancies of $d_{xy}$ and $d_{xz}$ are different as one moves along the c-axis, whereas that of $d_{x^2-y^2}$ remains the same in both AFM and FM phases. The orbital polarization increases on increasing the value of $U$ and alternates for the $d_{xz}$ and $d_{yz}$ orbitals (see, e.g., V1 and V2) in successive vanadium layers along the c-axis. This orbital order with alternating dominant occupancies of $d_{xz}$ and $d_{yz}$ orbitals can be clearly understood from the structural distortions observed in the equatorial V–O bonds (see the inset of figure 1). For example, the distortion observed for V1 along the a-axis is seen to appear along b for V2. This interchange of distortions along a- and b-axes results in alternate higher or lower occupancy of a particular orbital between V1 and V2. This is similar to an A-type antiferro-orbital order where the antiferromagnetic V chains parallel to the ab-plane have ferro-orbital order (e.g. similar orbital occupancies of V1 and V5 ions or those of V2 and V6 ions) whereas along the c-axis there is an antiferro-orbital

\begin{table}
\centering
\begin{tabular}{|l|c|c|c|c|c|c|c|c|c|}
\hline
Site & $d_{x^2-y^2}$ & $d_{xz}$ & $d_{yz}$ & $\mu_S$ & $d_{x^2-y^2}$ & $d_{xz}$ & $d_{yz}$ & $\mu_S$ \\
\hline
V1 (V3) & 0.665 & 0.553 & 0.386 & 1.53 & 0.677 & 0.656 & 0.438 & 1.60 \\
V5 (V7) & 0.665 & 0.553 & 0.386 & 1.53 & 0.677 & 0.656 & 0.438 & 1.60 \\
V2 (V4) & 0.665 & 0.386 & 0.553 & 1.53 & 0.676 & 0.438 & 0.656 & 1.60 \\
V6 (V8) & 0.665 & 0.386 & 0.553 & 1.53 & 0.676 & 0.438 & 0.656 & 1.60 \\
\hline
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\begin{table}
\centering
\begin{tabular}{|l|c|c|c|c|c|c|c|c|}
\hline
Site & $d_{x^2-y^2}$ & $d_{xz}$ & $d_{yz}$ & $\mu_S$ & $d_{x^2-y^2}$ & $d_{xz}$ & $d_{yz}$ & $\mu_S$ \\
\hline
V1 (V3) & 0.595 & 0.451 & 0.591 & 1.571 & 0.603 & 0.556 & 0.540 & 1.65 \\
V5 (V7) & 0.595 & 0.451 & 0.591 & 1.571 & 0.603 & 0.556 & 0.540 & 1.65 \\
V2 (V4) & 0.759 & 0.214 & 0.665 & 1.571 & 0.795 & 0.272 & 0.621 & 1.65 \\
V6 (V8) & 0.759 & 0.214 & 0.665 & 1.571 & 0.795 & 0.272 & 0.621 & 1.65 \\
\hline
\end{tabular}
\end{table}
order between $d_{xz}$ and $d_{yz}$ orbitals (see occupancies of V1 and V2 or those of V5 and V6 in table 2). These orbital occupancies can also be obtained from the density matrix (calculated within the LSDA + $U$) diagonalization. This is consistent with the previous theoretical observation on the same system [13]. The observed intra-chain ferro-orbital order is also consistent with experimental antiferromagnetic order as per Goodenough–Kanamori–Anderson rules [19]. The orbital order described above is also revealed in the calculated real space electron density at each V site shown in figure 3. This orbital order is similar to the observation of Tsunetsugu and Motome [3] for vanadium spinels using a Kugel–Khomskii kind of model in the strong coupling limit. Interestingly, the orbital orders are found to be qualitatively similar in both FM and AFM phases within LSDA + $U$ (see table 2).

It would be interesting to compare at this point the orbital order obtained for MgV$_2$O$_4$ within LSDA + $U$ with that obtained for ZnV$_2$O$_4$ [5] and MnV$_2$O$_4$ [11] within the same approximation. While A-type antiferro-orbital order was observed in ZnV$_2$O$_4$, with the second vanadium electron occupying an orbital with symmetry $d_{xz} + d_{yz}$ in alternate $ab$-planes along the $c$-axis, a ferro-orbital order was observed for MnV$_2$O$_4$, with the $d_{yz}$ orbital being dominantly occupied by the second vanadium electron at each site. In MgV$_2$O$_4$ also we see an A-type antiferro-orbital order (as discussed above), but the difference with ZnV$_2$O$_4$ is that $d_{xz}$ and $d_{yz}$ orbitals are unequally occupied and the occupancies of these two orbitals alternate when one moves along the $c$-axis (see table 2). These orbital orders are directly connected to the cooperative Jahn–Teller distortions observed in the VO$_6$ octahedra in the respective systems in their low temperature tetragonal phases as described later.

As mentioned earlier, the influence of spin–orbit coupling on the magnetic and orbital order in these systems is continuously debated, but no consensus has been reached yet. In order to investigate the effect of spin–orbit interaction in this particular system, we also performed a more refined calculation with spin–orbit coupling within the LSDA + $U$ + SO approximation. The AFM phase continues to be energetically favored over the FM phase, within LSDA + $U$ + SO as well (see table 1). The partial DOS, shown for the AFM phase (figure 2(c)), clearly shows a non-negligible impact of SO in general, with an increased energy gap compared to that with LSDA + $U$. The analysis of orbital occupancies in this case indeed leads to some important and interesting observations. With finite spin–orbit coupling, the apparent degeneracy of $d_{xz}$ and $d_{yz}$ orbitals observed within LSDA + $U$ is no longer present and there is different occupancy for all the $t_{2g}$ orbitals (see table 2). Even though, as for LSDA + $U$, the antiferromagnetic V chains parallel to the $ab$-plane are still ferro-orbitally ordered and along the $c$-axis these chains are antiferro-orbital ordered, the orbital polarizations in adjacent chains along the $c$-axis are significantly different in the presence of SO interaction. For example, if we compare the occupancies (table 2) for V1 and V2 with LSDA + $U$ and LSDA + $U$ + SO, we note that orbital occupancies of $d_{xz}$ and $d_{yz}$ are no longer the same in the presence of SO interaction. Furthermore, the polarization of the $d_{xz}$ and $d_{yz}$ orbitals is also very different (e.g. at V2 the polarization of the $d_{yz}$ orbital w.r.t. $d_{xz}$ is much stronger than that at V1). This implies that V chains in successive layers along the $c$-axis are affected differently by the SO interaction. This is also reflected in the orbital moments of V ions (listed in table 3 and depicted in figure 4). The calculated electronic density at each V site shown in figure 3(b) brings out the impact of SO interaction. Both FM and AFM phases are associated with an orbital order where the adjacent V chains are differently affected by the SO interaction as shown in figure 3(b). Comparison of the total energies of the two solutions mentioned above shows that the latter is more stable and is lower in energy by 0.108 eV/f.u.

In figure 4 we show two successive vanadium chains along the $c$-axis in the AFM phase with the calculated electron density at each vanadium site in the presence of both Coulomb correlation and SO interaction. We have also marked the
interaction in MgV−V6 out of the six V−O bonds in the VO6 octahedron, two orbital moments are also shown qualitatively below each chain.

Table 3. Calculated orbital moment ($\mu_L$) and total magnetic moment ($\mu_S$) in $\mu_B$, and angle (in degrees) of $\mu_L$ w.r.t. z-axis within LSDA + U + SO for the AFM phase. $\mu_S$ is along the z-axis and is listed in table 2.

|       | x    | y    | z    | $\mu_L$ | Angle |
|-------|------|------|------|---------|-------|
| V1    | −0.355 | 0.000 | −0.466 | 1.15 | 17.79 |
| V5    | −0.355 | 0.000 | 0.466  | −1.15 | 162.21 |
| V2    | −0.015 | −0.030 | −0.510 | 1.05 | 1.90  |
| V6    | −0.015 | −0.030 | 0.510  | −1.05 | 178.10 |

direction of orbital and magnetic moments at each site. The effects of SO interaction are clearly different on the two chains and so are the arrangements of the orbital moments. One chain shows the canted orbital arrangement and the orbital moments are making an angle of 17.79° with the c-axis, whereas in the other chain the orbital moments make an angle of 1.90° (almost collinear orbital arrangement) with the c-axis (table 3). On one chain (V1–V5–V1–V5) due to canting of the orbital moment the effect of SO interaction reduces, whereas in the other chain orbital moments align almost opposite to the spin magnetic moment, implying a substantial SO interaction (as also reflected by the values listed in tables 2 and 3). The observation that the SO interaction appears to affect alternate V chains along the c-axis differently is interesting. This also substantiates the speculation of Wheeler et al [1] that SO interaction in MnV2O4 may not be as large as that in ZnV2O4 or as small as that in MnV2O4, as discussed earlier. The effect of SO coupling on orbital moments is small in MgV2O4 as compared to ZnV2O4. The magnitude of orbital moments observed in our calculation also corroborates this fact.

At this point it would be interesting to compare the structural distortions and the symmetries of ZnV2O4, MgV2O4 and MnV2O4 in their respective low temperature tetragonal phases. All these compounds undergo tetragonal compression along the c-axis with $c/a$ ratios 0.9948, 0.9941 and 0.98, respectively [7, 1, 8]. Apart from this compression, there are other structural distortions also present. In ZnV2O4, out of the six V−O bonds in the VO6 octahedron, two apical ones are shorter than the four equatorial V−O bonds. In MnV2O4, the four equatorial V−O bonds are further split into two groups where two are shorter and two are longer. In MgV2O4, there are four types of V−O bonds observed (inset of figure 1), with apical V−O bonds having unequal lengths. Furthermore, the trigonal distortion (where O−V−O angles in the VO6 octahedron deviate from 90°) is also present in all three compounds with varying strength. These features are reflected in their crystal symmetries. The tetragonal ZnV2O4 has $I4_1/amd$ symmetry, whereas MgV2O4 and MnV2O4 have $I4_1/m$ and $I4_1/a$ symmetries, respectively. While ZnV2O4 preserves both mirror and glide symmetries, MgV2O4 has only mirror symmetry and MnV2O4 has neither mirror nor glide symmetry in its low temperature phase. The different symmetries in the three compounds signify that the orbital order should also be consistent with the corresponding symmetries and hence could have different origins. As the magnetic exchange interactions depend on the character of the occupied orbitals, the low temperature magnetic order is also coupled to the orbital order. So the competition among tetragonal distortion, trigonal distortion and spin–orbit interaction decides the symmetries of the occupied orbitals and hence the orbital order in the system.

Our results show that a small but non-negligible spin–orbit coupling, along with the significant trigonal distortion present in MgV2O4, has a substantial effect on the orbital order of this system. This observation is consistent with the experimental observations by Wheeler et al [1] of antiferromagnetic chains with a strongly reduced moment and the one-dimensional behavior and a single band of excitations projected by the inelastic neutron scattering.

4. Conclusions

To conclude, we have studied the effect of spin–orbit interaction on magnetic and orbital order in the low temperature tetragonal phase of MgV2O4. We observe that, even though the orbital moments are relatively small compared to those of ZnV2O4, the orbital order in successive vanadium chains is differently affected in the presence of SO interaction. In one chain (V1–V5–V1–V5) the three orbitals $d_{x^2−y^2}$, $d_{yz}$ and $d_{xz}$ are nearly equally populated, giving rise to a canted (non-collinear) arrangement of orbital moments, whereas in the other (V2–V6–V2–V6) the orbitals are highly polarized, leading to an almost collinear arrangement of orbital moments. These results imply that SO interaction in MgV2O4 is non-negligible and has a significant effect on orbital order. However, it is not very strong, unlike the case of ZnV2O4, and at the same time not very weak, unlike the case of MnV2O4. The orbital order, namely the structural distortions in these compounds, is also discussed.

Acknowledgments

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