Role of orbital degrees of freedom in investigating the magnetic properties of geometrically frustrated vanadium spinels

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ABSTRACT

The inconsistency about the degree of geometrical frustration has been a long issue in AV_2O_4 (A ≡ Zn, Cd and Mg) compounds, which arises from the two experimental results: (i) frustration indices and (ii) magnetic moments. In the present study, we try to understand such inconsistency by using *ab initio* electronic structure calculations. The orbital degrees of freedom are found to play an important role in understanding the geometrically frustrated magnetic behavior of these compounds. The magnitude of the maximum calculated values of orbital magnetic moment per formula unit for ZnV_2O_4, MgV_2O_4 and CdV_2O_4 compounds are found to be ~1.54 μ_B, ~0.92 μ_B and ~1.74 μ_B, respectively. The inclusion of the orbital and spin angular momenta for calculating the frustration indices improves the understanding about the degree of geometrical frustration in these compounds. The calculated values of the frustration indices (f_J) are largest for MgV_2O_4 and smallest for CdV_2O_4 for $3.3 \leqslant U \leqslant 5.3$ eV. In this range of U, the calculated values of $\Delta M_2 = M_{total} - M_{exp}$ (where, $M_{total} = M_{spin} - |M_{orbital}|$) are also found to be largest for MgV_2O_4 and smallest for CdV_2O_4. Hence, the consistency about the degree of geometrical frustration, which arises from the f_J as well as from the ΔM_2 is achieved and improves the understanding about the degree of geometrical frustration in these compounds. Calculated values of band gap in this range of U are found to be closer to that of experimentally observed values for all three compounds. The absolute values of the nearest neighbor exchange coupling constant (J_{nn}) between V spins are found to be largest for MgV_2O_4 and smallest for CdV_2O_4, which indicate that the calculated absolute values of the Curie-Weiss temperature $(\Theta_{CW})_J$ are highest for MgV_2O_4 and smallest for CdV_2O_4 for $3.3 \leqslant U \leqslant 5.3$ eV. In this range of U, the magnetic transition temperature $(T_N)_J$ is found to be ~150 K, ~60 K and ~22 K for MgV_2O_4, ZnV_2O_4 and CdV_2O_4, respectively, which shows that the order of $(T_N)_J$ is similar to that of $(T_N)_{exp}$ for these compounds. Hence, all the magnetic properties studied in the present work are well explained in these spinels for $3.3 \leqslant U \leqslant 5.3$ eV. This work is expected to provide a valuable input in understanding the geometrically frustrated magnetic behavior for those systems for which the orbital part of the angular momenta are not quenched.

1. Introduction

The ground state properties in the condensed matter physics have been well described from long time by the density functional theory (DFT) approach [1–3]. At least in the metallic systems, such properties are described well either by local density approximation (LDA) or generalized gradient approximation (GGA) based on the DFT. However, it is well known that these functionals underestimate the orbital moments for strongly correlated systems, which are induced by the strong spin orbit coupling (SOC) [4–7]. This

can be resolved by adding orbital dependent Hartree-Fock (HF) potential to the LDA/GGA, so called LDA+U/LDA+U approximation [7–10]. A major problem in this approach is that the electron-electron interaction has already been included in LDA/GGA potential. Hence, the simple addition of HF potential leads to double counting (DC). Here, the best way is to identify the mean-field-part of the HF potential and subtract it, leaving the orbital dependent correction to the mean field type LDA potential. Czyżyk and Sawatzky suggested a scheme that is true for uniform occupancies, so called around mean field (AMF) and is applicable to the weakly correlated systems [3]. For strongly correlated systems, AMF DC scheme is not valid due to the lack of uniform occupancies. For these systems, one can prefer the fully-localized (FL) DC scheme,

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where the average effect for a localized state is subtracted with integer occupation number [7,8].

Geometrical frustration is always a challenging problem in the strongly correlated systems. In these systems it arises due to the interactions between spin degrees of freedom in a lattice, which are incompatible to that of the essential crystal geometry. In the highly geometrically frustrated magnets, frustration suppresses the long-range magnetic order and leads to a degenerate manifold of ground states. Degeneracy in the frustrated magnetic systems yield different complex ordering structures, spin liquid states and spin ice states [11,12]. Charge ordering phenomena are also much affected by the geometrical frustration [13]. After 1980s, spin systems on the pyrochlore lattice (an example of geometrically frustrated structures) have been studied in more detail [12,14–20]. In the classical Heisenberg spin systems, a very strong geometrical frustration is anticipated due to the antiferromagnetically coupled spins on a pyrochlore lattice, which do not show long-range order at any nonzero temperature [12,19,20].

Vanadium spinels, AV_2O_4 (A ≡ Zn, Cd and Mg) with the face-centered-cubic structure at room temperature are an interesting example of geometrically frustrated systems, which show a variety of physical properties [21–31]. In these systems a pyrochlore lattice is formed due to the corner sharing network of tetrahedra with magnetically coupled V atoms that gives the geometrical frustration [30–37]. As opposed to the other geometrically frustrated systems, vanadium spinels show the long range antiferromagnetic ordering at low temperature [40]. In these compounds, orbital ordering is found to be responsible for the structural transition that leads to a long range magnetic ordering due to the lifting of geometrical frustration in the tetragonal structure [41,42]. The structural transition temperature (T_S) for CdV_2O_4 (~97 K) > MgV_2O_4 (~65 K) > ZnV_2O_4 (~50 K) compound [32–34,41,43–45]. However, the magnetic transition temperature (T_N) for MgV_2O_4 (~42 K) > ZnV_2O_4 (~40 K) > CdV_2O_4 (~35 K) compound [32–34,41,43–45]. The values of T_N for these compounds are always found to be less than T_S. However, it is expected that the values of T_S and T_N should be same for these compounds because the geometrical frustration is removed by the above proposed mechanism. The fact that $T_N < T_S$ in these compounds, indicates the presence of certain degree of geometrical frustration in the tetragonal phase of the compound.

The presence of geometrical frustration in the above mentioned compounds can be attributed to the following two experimental facts. First one is the frustration index, defined as $f_S = |\Theta_{CW}|/T_N$, where $|\Theta_{CW}|$ and T_N are the Curie-Weiss temperature and the magnetic ordering temperature, respectively. Experimentally reported values of Θ_{CW} for ZnV_2O_4, MgV_2O_4 and CdV_2O_4 are ~850 K, ~600 K and ~400 K, respectively [45,46]. However, in some literature these values are reported to be different for these compounds depending upon the experimental conditions [33,47–50]. In general, one can use the parameter f_S as a measure of strength of geometrical frustration in the system [27,40,45]. The values of f_S for ZnV_2O_4, CdV_2O_4 and MgV_2O_4 are found to be 21.3, 11.4 and 14.3, respectively [45]. Among these compounds, ZnV_2O_4 is largest frustrated and CdV_2O_4 is least frustrated as large value of f_S indicates the more frustration in the system. The second one is based on the difference between the spin magnetic moment per formula unit (MM/f.u.) [M_{spin}] and the experimentally observed MM/f.u. (M_{exp}), which is denoted by $\Delta M_1 = M_{spin} - M_{exp}$ in the antiferromagnetic phase of these compounds. M_{spin} for these compounds is found to be 4 μ_B. However, M_{exp} for CdV_2O_4, ZnV_2O_4 and MgV_2O_4 compounds are reported to be 2.38 μ_B, 1.26 μ_B and 0.94 μ_B, respectively [30,33,34,44]. Large values of ΔM_1 is explained in two different ways. One way of understanding is to attribute this difference to the activeness of geometrical frustration in these

compounds, which results in the quantum fluctuations responsible for the reduction of M_{exp} drastically as reported in MgV_2O_4 [44]. If this is the case, then the degree of the geometrical frustration for MgV_2O_4 > ZnV_2O_4 > CdV_2O_4. Also, the order of geometrical frustration that arises from the experimentally reported frustration index is found to be ZnV_2O_4 > MgV_2O_4 > CdV_2O_4 as described in Ref. [43]. Hence, both the results show the inconsistency about the degree of geometrical frustration in these compounds. Another way of understanding will be by considering contribution of the magnitude of orbital part of MM/f.u. (denoted by $|M_{orbital}|$) reported by Maitra et al. for ZnV_2O_4 [25]. The calculated values of the $|M_{orbital}|$ for ZnV_2O_4, MgV_2O_4 and CdV_2O_4 compounds are found to be ~1.50 μ_B, ~0.4 μ_B and ~0.4 μ_B, respectively [25,27,28]. Even by considering the $|M_{orbital}|$, the total calculated MM/f.u. (M_{total}) is still larger than the M_{exp}, indicating that the certain degree of geometrical frustration is still present in these compounds. The inclusion of $|M_{orbital}|$ does not improve the situation.

The above discussion clearly suggests that the current understanding of these compounds is not sufficient to resolve the contradiction about the degree of geometrical frustration present especially in ZnV_2O_4 and MgV_2O_4. In the present work we have tried to resolve this contradiction by carrying out detailed LDA+U +SOC calculations. Our results clearly show the importance of orbital degrees of freedom along with the spin in understanding the magnetic properties of these compounds. The inclusion of orbital and spin angular momenta for calculating the frustration indices improves the understanding about degree of geometrical frustration present in these compounds. The calculated values of the frustration indices f_J thus obtained for $3.3 \leqslant U \leqslant 5.3$ eV provide the largest value for MgV_2O_4 and smallest for CdV_2O_4. This behavior is similar to that expected from the ΔM_2. In this range of U, the magnitude of Curie-Weiss temperature [$(\Theta_{CW})_J$] are highest for MgV_2O_4 and smallest for CdV_2O_4, which indicate that the magnitude of the nearest neighbor exchange coupling constant (J_{nn}) among V spins are largest for MgV_2O_4 and smallest for CdV_2O_4 compounds. Also, the order of magnetic transition temperature [$(T_N)_J$] is found to be consistent with the experimentally reported order of magnetic transition temperature $(T_N)_{exp}$ for these spinels for above mentioned range of U.

2. Computational detail

In present work, the ferromagnetic (FM) and antiferromagnetic (AFM) electronic-structure calculations of AV_2O_4 (A ≡ Zn, Cd and Mg) compounds are carried out by using the *state-of-the-art* full-potential linearized augmented plane wave (FP-LAPW) method [51]. The atomic positions and lattice parameters used in the calculations for every compounds are taken from the literature [33,34,44]. All these calculations are performed in the tetragonal phase for which Perdew-Wang/Ceperley-Alder exchange correlation functional has been used [52]. In order to calculate the nearest neighbor exchange coupling constant (J_{nn}), we have considered the two magnetic orderings: FM and AFM (not the experimentally observed structure) ordering of the spins of the four V atoms in a primitive unit cell. For AFM ordering, the primitive unit cell consists of two up and two down spins on the four V atoms. The effect of on-site Coulomb interaction among V 3d electrons is considered within LDA+U formulation of the density functional theory [7]. Normally in this method U and J are used as parameters. However in our calculations, only U is used as a free parameter and the value of J is calculated self-consistently as described in Ref. [7]. FL and AMF DC schemes have been used in these calculations [3,8]. Both the DC schemes give the similar results. Thus in order to avoid the repetition of the results, we have discussed the results