Effect of pressure on the electronic and magnetic properties of CdV$_2$O$_4$: Density functional theory studies

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We investigate the effect of pressure on the electronic and magnetic states of CdV$_2$O$_4$ by using ab initio electronic structure calculations. The Coulomb correlation and spin-orbit coupling play important role in deciding the structural, electronic and magnetic properties of the compound. The total magnetic moment of V ion is found to be $~1.3 \mu_B$ and making an angle of $~9.5$ degree with the z-axis. In the tetragonal phase, the ground state is the orbital ordered state where V $d_{xz}$ and $d_{yz}$ orbitals are mainly occupied at the neighbouring sites. This work predicts the electronic phase transition from orbital-ordered-insulator to orbital-ordered-metal to orbital-disordered-metal with increasing pressure. The pressure induced broadening of lower and upper Hubbard bands gives rise to metal-insulator transition above 35 GPa. The simple mean-field theory used in the present work is able to describe the pressure dependent variation of the antiferromagnetic transition temperature suggesting the applicability of the method in the study of the magnetic behaviour of similar geometrically frustrated systems.

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I. INTRODUCTION

The spinel vanadates having general formula AV$_2$O$_4$ (A=Cd, Mg and Zn) offer a fertile ground to study many aspects of condensed matter physics. At room temperature they are paramagnetic insulator with face-centred cubic structure. The four V ions forming a regular tetrahedron and their spins are antiferromagnetically coupled resulting in an interesting example of a geometrically frustrated system. At low temperature they show structural transition from cubic to tetragonal and the tetrahedron becomes distorted as shown in Fig. 1. The four sites of the V atoms forming the tetrahedron are orbitally inequivalent as V1 and V2 atoms have different orbital occupancies. The magnetic transition from paramagnetic to antiferromagnetic (AFM) is also observed at lower temperature.

Among the above mentioned three compounds the structural transition temperature ($T_S$) is highest ($~97$ K) for CdV$_2$O$_4$ and lowest ($~50$ K) for ZnV$_2$O$_4$. On the other hand the AFM transition temperature ($T_N$) is lowest ($~35$ K) for CdV$_2$O$_4$ and highest ($~42$ K) for MgV$_2$O$_4$. The frustration index, defined as $f \equiv \theta_{CW}/T_N$ where $\theta_{CW}$ is the Curie-Weiss temperature and $T_N$ is the AFM transition temperature, is considered as a measure of the activeness of geometrical frustration. The values of $f$ for CdV$_2$O$_4$, MgV$_2$O$_4$, and ZnV$_2$O$_4$ compounds are found to be about 11.4, 14.3, and 21.3, respectively, suggesting that the geometrical frustration is least active in CdV$_2$O$_4$. The pressure dependent magnetization studies on CdV$_2$O$_4$ and ZnV$_2$O$_4$ have been carried out by Canosa et al. and found opposite trends for the $T_N$. The $T_N$ of CdV$_2$O$_4$ and ZnV$_2$O$_4$, respectively, increases and decreases with increase in pressure. These contrasting behaviours in this series of compounds are unusual and yet to be understood.

It is clear from the above discussion that CdV$_2$O$_4$ is a relatively simple compound where the effect of spin fluctuations due to geometrical frustration is expected to be minimal. Thus CdV$_2$O$_4$ would be a good starting candidate to study the complex physical properties of the above compounds using density functional theory (DFT), which is a mean-field theory. Here we employ the DFT based ab initio electronic structure calculations to study the pressure dependent electronic and magnetic properties of CdV$_2$O$_4$ compound. The Coulomb correlation among V 3d electrons are found to be important in understanding its structural and electronic properties. The spin-orbit coupling (SOC) is weak and total magnetic moment of the V ion comes out to be $~1.3 \mu_B$ which is closer to the experimental value of $~1.2 \mu_B$. It shows orbital ordered ground state where $d_{xz}$ and $d_{yz}$ orbitals are mainly occupied at the neighboring V sites. The electronic states of the compound evolves from orbital-ordered-insulator to orbital-ordered-metal to orbital-disordered-metal with increasing pressure. The broadening of lower and upper Hubbard bands due to increasing pressure is found to be responsible for the pressure induced metal-insulator transition. The present mean-field calculations correctly describe the pressure dependent shift of $T_N$ indicating the applicability of such approach in understanding the magnetic properties of similar systems.

II. COMPUTATIONAL DETAILS

The ferromagnetic (FM) and AFM calculations of CdV$_2$O$_4$ have been carried out by using state-of-the-art full-potential linearized augmented plane wave (FP-LAPW) method. In the AFM solution the directions of
spins of V1 and V2 atoms shown in Fig. 1 are considered to be opposite. The muffin-tin sphere radii used in the present work are 2.0, 1.85, and 1.52 Bohr for Cd, V, and O atoms, respectively. In order to see the effect of pressure on the electronic and magnetic properties of the compound only volume of the primitive unit cell is varied. The atomic positions and tetragonal distortion are kept fixed to the reported experimental values of 85 K. The effect of on-site Coulomb interaction among V 3d electrons is also considered within GGA+U formulation of the DFT. The values of U and J used in the calculations are 4.0 and 0.5 eV, respectively, which were found to describe the correct electronic and magnetic properties of MgV₂O₄ compound. The self-consistency was achieved by demanding the convergence of the total energy to be smaller than 10⁻⁵ Hartree/cell. To study the role of orbital degree of freedom in deciding the magnetic properties of the compound the spin-orbit coupling (SOC) is also considered. The initial axis of magnetization was set along the z-axis and convergent solution was obtained in presence of SOC, which corresponds to a non-collinear magnetism. The consideration of SOC in the calculation is very time consuming, therefore for this solution the energy convergence criterion was set to be smaller than 10⁻⁴ Hartree/cell.

III. RESULTS AND DISCUSSIONS

The energy vs volume plots of CdV₂O₄ obtained from FM and AFM GGA+U calculations are show in Fig. 2. Both the curves show almost parabolic behaviour and the volume corresponds to minimum energy is found to be around 1092 Bohr³. The energy of AFM solution is always found to be less than that of FM solution suggesting the AFM ground state of the compound for the range of unit cell volumes studied here. The energy difference between FM and AFM phase increases with decrease in volume. Thus decrease in volume gives rise to more stability to the AFM phase in comparison to FM phase. In order to know the exact equilibrium volume of the compound we fitted the energy-volume data by using equation of states formula of Vinett et al. The equilibrium volumes thus obtained correspond to FM and AFM solutions are 1096.6 and 1093.1 Bohr³, respectively, which are about 1% and 1.3% less than the experimental value of 1108.2 Bohr³ at 85 K. The bulk moduli of the compound found for FM and AFM solutions are ~180.8 and ~170.7 GPa which is about 0.4 times less than the bulk modulus of diamond. For U=5 eV the equilibrium volume and bulk modulus of the ground state AFM phase is found to be about 1098.4 Bohr³ and 175.5 GPa, respectively, suggesting that the increased value of U does not have much influence on its structural properties. The present calculated value of the bulk modulus is about 20 GPa more than that reported earlier and obtained from the use of hybrid functional.

The partial density of states (PDOS) of Cd 4d, V 3d and O 2p states obtained from FM GGA+U solution corresponding to equilibrium volume are shown in Fig. 3. The valence band can be divided in three regions: (i) region A from 0 to -2.0 eV, (ii) region B from -2.2 to -7.8 eV and (iii) region C below -7.8 eV. Regions A and C are dominated by V 3d and Cd 4d states, respectively, whereas region B has similar contribution from all the three atoms. The shape of Cd 4d, V 3d and O 2p PDOS are similar in all the regions suggesting the hybridization between Cd 4d, V 3d and O 2p orbitals. The lowest lying conduction bands, denoted by 1 and 2 in Fig. 3(b), have dominating contribution from V 3d states. There is a finite gap between regions A and B which can be attributed to the gap between bonding and antibonding bands arising due to finite overlap of V 3d and O 2p orbitals. The band gap of ~0.3 eV is essentially arising due to correlation induced splitting of V 3d bands in lower and upper Hubbard bands putting this compound into the category of Mott-Hubbard insulator.

In order to know the exact magnetic moment (MM) of the V ion we have included SOC in the calculation and obtained the FM solution. The spin part of MM at the V site is found to be about 1.6 µB and directed along the z-axis. The total spin only MM is found to be 2 µB per formula unit (fu) suggesting that effectively V ion is in S=1 ground state as expected for 3+ ionic state of the V in this compound. The total magnetic moment is mainly lying in the yz-plane. The y and z components of the orbital moment (L) are found to be about -0.1 and -0.2 respectively where negative sign indicates the direction of the moment. Since the direction of the spin moment (S) is mainly along the z-axis. Thus the total moment (J) also lies in the yz-plane. The y and z components of J are found to be about -0.1 and 0.6. Using these values of L, S and J one can estimate the magnitude and direction of total magnetic moment of V ions. The magnitude comes out to be ~1.3 µB, which is in good agreement with the experimental value of about 1.2 µB. The total magnetic moment is making an angle of ~9.5 degree with the z-axis. Here it is important to note that there is a large difference between the calculated and experimentally observed MM of MgV₂O₄ compound and this behaviour has been attributed to the activeness of geometrical frustration responsible for quantum fluctuations. However, the small difference of 0.1 µB between the calculated and experimental MM for CdV₂O₄ suggests that the geometrical frustration may be less important for understanding its magnetic properties. This observation can further be justified by comparing the frustration index f of both the compounds. The values of f for CdV₂O₄ and MgV₂O₄ have been reported to be 11.4 and 14.3, respectively, suggesting that geometrical frustration is less active in the CdV₂O₄. Finally one should keep in mind that the DFT is a mean-field theory and effect of quantum fluctuations can not be studied using this technique. Therefore, in the geometrically frustrated system the difference
between the experimental and calculated magnetic moment is expected; and it can be directly related to the $f$. Since the value of $f$ for MgV$_2$O$_4$ is greater than that of CdV$_2$O$_4$, therefore the difference between the experimental and calculated magnetic moment for MgV$_2$O$_4$ is expected to be more in comparison to CdV$_2$O$_4$ as mentioned above.

The electronic occupancy of $d_{zz}$ ($d_{yz}$) orbital for two vanadium atoms V1 and V2 forming the tetrahedron (see Fig. 1) is found to be about 0.79 and 0.06 (0.06 and 0.79), respectively. The occupancies of rest of three V 3d orbitals are same at each V sites. This result clearly shows the orbital ordered ground state for the CdV$_2$O$_4$ compound where $d_{zz}$ and $d_{yz}$ orbitals are mainly occupied at V1 and V2 sites of the tetrahedron. Here it is important to note that the AFM solution does not have much influence on the orbital ordering and solely arising due to tetragonal structure of the compound.

The evolution of electronic structure of the compound with increasing pressure is shown in Fig. 4, where we have plotted total density of states (TDOS) per formula unit (fu) obtained from AFM solutions at different pressure. One can notice couple of obvious changes in the TDOS with varying pressure. With increasing pressure Cd 4d states are becoming deeper in energy. The gap between regions A and B enhances with increasing pressure suggesting the increased energy difference between the bonding and antibonding molecular orbitals mainly consist of V 3d and O 2p atomic orbitals. This behaviour is as per the expectation because increasing pressure increases the overlap between V 3d and O 2p atomic orbitals and the energy difference between bonding and antibonding molecular orbitals is proportional to the overlap between the atomic orbitals. With increase in pressure the band gap decreases from $\sim$0.5 to $\sim$0.27 eV at 16.6 GPa as conduction band (CB) 1 comes closer to the valence band (VB). The gap almost vanishes at 34.5 GPa as the maximum of VB and minimum of CB 1 merges with each other as evident from Fig. 4(c). On further increase of pressure the VB and CB 1 started overlapping and such overlap of VB and CB may lead to metallic conductivity above 34.5 GPa. The TDOS/fu at the Fermi level increases from $\sim$1 states/eV at 87.5 GPa to $\sim$2 at 105.5 GPa enhancing the conductivity by 2 times. Dispersion relations along high symmetric directions of the Brillouin zone for 0.23 and 34.5 GPa are shown in Fig. 5. It is evident from Fig. 5(a) that the valence band maximum and conduction band minimum lie at the $Z$ point and $\Gamma$ point, respectively. The energy difference between these two points gives the indirect band gap of $\sim$0.5 eV, which is responsible for the insulating behaviour of the compound. When pressure is increased to 34.5 GPa the energy difference between the $Z$ and $\Gamma$ points becomes almost zero. This suggests the pressure induced insulator to metal transition above 34.5 GPa. The increase in pressure brings V atoms closer resulting in increased overlap between V 3d orbitals. This finally leads to broadening of upper and lower Hubbard bands giving rise to reduced separation between them which is responsible for the decrement in the gap with increasing pressure. Thus present work clearly indicates the pressure induced metal-insulator transition in the compound due to broadening of upper and lower Hubbard bands.

To study the effect of pressure on the orbital ordering we have plotted the pressure dependent electronic occupancies of V $d_{zz}$ and $d_{yz}$ orbitals at V1 sites obtained from AFM solutions in Fig. 6. The degree of orbital polarization at V1 sites can be defined as $P_{orb} = (d_{zz} - d_{yz})/(d_{zz} + d_{yz})$. $P_{orb} = 1$ corresponds to 100% orbital polarization as only $d_{zz}$ orbital is occupied at V1 sites. Needless to say that this situation automatically tells about 100% orbital polarization at V2 sites where only $d_{yz}$ orbital is occupied. $P_{orb} = 0$ corresponds to orbital disordered state as same kind of orbitals will be occupied at every sites. The occupancies of both the orbitals show almost linear pressure dependence in the insulating region and non-linear pressure dependence in the metallic region. The occupancy of $d_{zz}$ continuously decreases with increase in pressure. The pressure dependent occupancy of $d_{yz}$ orbital shows non-monotonous behaviour. It decreases in the insulating region and increases in the metallic region. The $P_{orb}$ also shows non-monotonous pressure dependence. In the insulating phase the value of $P_{orb}$ increases slowly from $\sim$0.46 at 0 GPa to $\sim$0.52 at 34.5 GPa. However, the decrement of $P_{orb}$ is fast in the metallic phase as its value reduces from $\sim$0.51 at 71.6 GPa to $\sim$0.32 at 105.5 GPa. This result suggests the complete melting of the orbital ordering at higher pressure. Thus, the present work clearly shows the interesting pressure evolution of the electronic state of CdV$_2$O$_4$ from orbital-ordered-insulator to orbital-ordered-metal and then to orbital-disordered-metal with increasing pressure in the tetragonal structure.

As opposed to the electronic state, the magnetic state of the compound is found to be robust with increasing pressure as the MM of the V ion remains almost the same even at 105.5 GPa. In order to know the effect of pressure on the magnetic transition temperature we have plotted the Heisenberg exchange parameter $J$ of neighbouring V ions as a function of pressure in Fig. 7. The pressure dependence values of $J$ have been estimated by mapping of energies of FM and AFM solutions to the Heisenberg Hamiltonian and assuming that only neighbouring V ions have strong magnetic interactions. Keeping the localized nature of V 3d orbitals in mind it may be considered as a fairly good approximation. The $J$ shows almost linear pressure dependence and it increases with increasing pressure indicating the enhanced exchange interaction strength due to increased overlap of V 3d orbitals. If we scale the $J$ with experimental $T_N$ then $J$ at zero pressure is equivalent to $T_N$ at zero pressure. Using this scaling one can plot the pressure dependence of $T_N(P)/T_N(0)$. For the direct comparison with the experimental data shown in Fig. 3 of Ref. 16, we have shown the interpolated value of $T_N(P)/T_N(0)$ up to 10 Kbar in
the inset of Fig. 7. Our result shows about 2.5% increase in \( T_N \) per GPa (i.e. 10 Kbar) of pressure which is closer to the experimental observation. Keeping the complex nature of magnetic transition in mind where spin fluctuations due to geometrical frustrated can not be fully ignored, the applicability of such a simple mean-field approach in understanding the pressure dependent shift in the \( T_N \) is quite interesting and demands further investigation to such similar systems.

IV. CONCLUSIONS

The effect of pressure on the electronic and magnetic properties of tetragonal \( \text{CdV}_2\text{O}_4 \) have been studied by using GGA+\( U \) formulation of the density functional theory. The present study shows the importance of on-site Coulomb interaction among the V 3\( d \) electrons in deriving the insulating ground state of the compound. The spin-orbit coupling is weak and responsible for titling the total magnetic moment \( \sim 1.3 \mu_B \) of the V ion by \( \sim 9.5 \) degree with the \( z \)-axis. The \( d_{xz} \) and \( d_{yz} \) orbitals are found to be mainly occupied at neighboring V sites. The electronic structure of the compound shows interesting evolution from orbital-ordered-insulator to orbital-ordered-metal to orbital-disordered-metal with increasing pressure. The pressure induced metal-insulator transition is essentially arising due to broadening of lower and upper Hubbard bands. The present work clearly demonstrates the applicability of the mean-field theory in understanding the pressure dependent behaviour of the magnetic transition temperature in similar geometrically frustrated systems.

V. FIGURE CAPTIONS:

FIG. 1. (Color online) Atomic arrangement in the primitive unit cell. The tetrahedron contains four V atoms denoted by V1 and V2. V1 and V2 are orbitally inequivalent sites.

FIG. 2. (Color online) Energy vs volume plots of FM and AFM solutions obtained from GGA+\( U \) (\( U=4 \) eV) calculations.

FIG. 3. (Color online) Partial density of states (PDOS) for (a) \( \text{Cd} \) 4\( d \), (b) V 3\( d \), and (c) O 2\( p \) symmetric states obtained from FM solution. Zero in the energy axis indicates the Fermi level.

FIG. 4. (Color online) The total density of states (TDOS) per formula unit (fu) obtained from AFM solutions at 0.23, 16.6, 34.5, 45.3, 87.5, and 105.5 GPa are shown in figures (a), (b), (c), (d), (e), and (f), respectively. Zero in the energy axis indicates the Fermi level.

FIG. 5. (Color online) Dispersion relations along high symmetric directions of the Brillouin zone for AFM solutions obtained for (a) 0.23 GPa and (b) 34.5 GPa.

FIG. 6. (Color online) The electronic occupancies of V \( d_{xz} \) and \( d_{yz} \) orbitals along with orbital polarization \( P_{\text{orb}} = (d_{xz} - d_{yz})/(d_{xz} + d_{yz}) \) for V1 sites is shown as a function of increasing pressure. The insulating and metallic regions

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22 The volume quoted here is the volume of primitive unit cell containing two formula unit whereas volume given in Ref. 18 is the volume of conventional unit cell containing 4 formula unit.
FIG. 7. (Color online) The Heisenberg exchange parameter ($J$) for neighbouring V ions at different pressure obtained from GGA+$U$ ($U=4$ eV) calculations. The inset shows the pressure dependence of $T_N(P)/T_N(0)$ obtained from the scaling of the $J$. See the text for details.
Cd $4d$

V $3d$

O $2p$
(a) 0.23 GPa
(b) 16.6 GPa
(c) 34.5 GPa
(d) 45.3 GPa
(e) 87.5 GPa
(f) 105.5 GPa

TDOS (states eV\(^{-1}\) fu\(^{-1}\))

Energy (eV)
$J$ (meV) vs. Pressure (GPa)

Inset: $T_N(P)/T_N(0)$ vs. $P$ (Kbar)

$T_N(P)/T_N(0)$ vs. Pressure (GPa)