Electronic structure study of vanadium spinels by using density functional theory and dynamical-mean-field theory

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Abstract – Theoretically, various physical properties of AV$_2$O$_4$ (A = Zn, Cd and Mg) spinels have been extensively studied for last 15 years. Besides this, no systematic comparative study has been done for these compounds, where the material specific parameters are used. Here, we report the comparative electronic behaviour of these spinels by using a combination of density functional theory and dynamical-mean-field theory, where the self-consistent calculated Coulomb interaction $U$ and Hund’s coupling $J$ (determined by the Yukawa screening $\lambda$) are used. The main features, such as insulating band gaps ($E_g$), degree of itinerancy of V $3d$ electrons and position of the lower Hubbard band, are observed for these parameters in these spinels. The calculated values of $E_g$ for ZnV$_2$O$_4$, CdV$_2$O$_4$ and MgV$_2$O$_4$ are found to be $\sim$0.9 eV, $\sim$0.95 eV and $\sim$1.15 eV, respectively, where the values of $E_g$ are close to the experiment for ZnV$_2$O$_4$ and MgV$_2$O$_4$. The position of the lower Hubbard band are observed around $\sim$ −1.05 eV, $\sim$ −1.25 eV and $\sim$ −1.15 eV for ZnV$_2$O$_4$, CdV$_2$O$_4$ and MgV$_2$O$_4$, respectively, which are also in good agreement with the experimental data for ZnV$_2$O$_4$. The order of the average impurity hybridization function of the V site are found to be ZnV$_2$O$_4$ > MgV$_2$O$_4$ > CdV$_2$O$_4$. Hence, the degree of localization of V $3d$ electrons is largest for CdV$_2$O$_4$ and smallest for ZnV$_2$O$_4$, which is in accordance with our earlier results. Hence, the present work shows the importance of material-specific parameters to understand the comparative electronic behaviour of these compounds.

Introduction. – Strongly correlated vanadium spinels, AV$_2$O$_4$ (A = Zn, Cd and Mg), have been thoroughly studied both theoretically and experimentally because of the presence of a large variety of physical properties such as electronic, structural and magnetic, etc. [1–14]. At room temperature, these compounds show face-centered-cubic (FCC) structure. Geometrical frustration is seen in the anti-ferromagnetically coupled V ions with spin $S = 1$ residing on the vertices of corner-sharing tetrahedra forming a pyrochlore lattice [3–6,8]. In this system, the interplay of spin, electron, orbital and lattice degrees of freedom leads to two successive phase transitions. The structural and magnetic transition takes place from cubic to tetragonal and paramagnetic to anti-ferromagnetic, respectively [1,2,10]. The structural (magnetic) transition temperature $T_S$ ($T_N$) for ZnV$_2$O$_4$, MgV$_2$O$_4$, and CdV$_2$O$_4$ is $\sim$50 K ($\sim$40 K), $\sim$65 K ($\sim$42 K) and $\sim$97 K ($\sim$35 K) [1,2,10,15]. However, their Curie-Weiss temperature is found to be much higher than the room temperature [15]. $T_S > T_N$, indicates that a certain degree of geometrical frustration is still present in these systems. The degree of geometrical frustration is measured by the frustration index, which is the ratio of the Curie-Weiss temperature and $T_N$. The frustration index is largest for ZnV$_2$O$_4$ (21.3) and lowest for CdV$_2$O$_4$ (11.4) as compared to MgV$_2$O$_4$ (14.3) [15]. The experimentally observed magnetic moment per V atom (band gap) for ZnV$_2$O$_4$, MgV$_2$O$_4$ and CdV$_2$O$_4$ is $\sim$0.63 $\mu_B$ ($\sim$0.32 eV, $\sim$1.1 eV), $\sim$0.47 $\mu_B$ ($\sim$0.36 eV, $\sim$1.08 eV) and $\sim$1.19 $\mu_B$ ($\sim$3.16 eV), respectively [1,2,10,16,17]. Normally the degree of localization of electrons is measured by the ratio of the transfer integral ($t$) between a neighbouring site and the Coulomb

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interaction $U$. Canosa et al. have argued qualitatively the order of the degree of localization of electrons of a V site for CdV$_2$O$_4$ > ZnV$_2$O$_4$ > MgV$_2$O$_4$ [18], while we have shown quantitatively in an earlier paper that the degree of localization of electrons of a V site is largest for CdV$_2$O$_4$ and smallest for ZnV$_2$O$_4$ [19].

In order to understand the various physical properties as mentioned above for these compounds, several groups have proposed different mechanisms [3–7, 9, 11–13, 20, 21]. Most of these mechanisms are based on the model calculations, which are fully parameters dependent. Similarly, some density functional theory (DFT)+$U$ electronic-structure calculations have also been performed in these systems, where normally $U$ and $J$ are used as adjustable parameters. By adjusting these parameters, different groups have explained the various experimentally observed properties in these systems [9, 11, 12, 22]. There is no systemically comparative study of these compounds available in the literature, where the parameters, $U$ and $J$ are material specific. Also, the limitations of this method have been clearly observed, if one want to understand the spectral properties of strongly correlated systems. This is because of its naturally static treatment of the electronic correlation. For example, this method fails to reproduce the experimentally reported quasiparticle peak of the $5f$ character of δ-Pu near the Fermi level [23]. Hence, in order to reproduce the spectral and thermodynamic properties of strongly correlated materials, more sophisticated methods are needed to account for the correlation effects beyond this method. The most successful method is the dynamical-mean-field theory (DMFT), which describes the correlation effects in a periodic lattice by a strongly interacting impurity coupled to a self-consistent bath [24, 25]. Merging this with the DFT method, the DFT+DMFT approach provides more material-specific predictions of correlation effects in solids [26–30]. Despite the many success of this method, Wang et al. and Dang et al. have shown that the Mott insulating state in early and late transition metal oxides are described by fine tuning of several parameters, including double counting (DC) and interaction $U$ [31, 32]. However, recently Haule et al. have developed a method where no fine tuning of the parameters is required to predict the Mott gaps in early transition metal oxides. They have shown that for a fixed value of $U$, Mott gaps of the order of experimental data are observed for these compounds [33].

From the above discussion, it is clear that none of the groups has applied the DFT+DMFT method in the strongly correlated vanadium spinels even in spite of having the limitations of the DFT+$U$ method as mentioned above. Here, in the present work we try to understand the comparative electronic behaviour of strongly correlated vanadium spinels by using the DFT+DMFT method, where the self-consistently computed material-specific parameters are used. For ZnV$_2$O$_4$ and MgV$_2$O$_4$, the calculated values of $E_g$ are in good agreement with the experimental data. Among these spinels, the average impurity hybridization function of the V site is largest for ZnV$_2$O$_4$ and smallest for CdV$_2$O$_4$. Hence the order of the degree of localization is found to be CdV$_2$O$_4$ > MgV$_2$O$_4$ > ZnV$_2$O$_4$, which is consistent with our earlier reported data. The position of the lower Hubbard band observed in the present study is also consistent with the experimental data for ZnV$_2$O$_4$.

### Computational details.

The paramagnetic electronic-structure calculations of vanadium spinels carried out in the FCC phase have been divided into two parts, DFT and DFT+DMFT. The DFT part of the calculations is performed by using the full-potential linearized augmented plane-wave (FP-LAPW) method as implemented in the WIEN2K code [34]. The exchange-correlation functional has been treated within the GGA of PBEsol [35]. The experimentally observed crystal structures for these spinels are taken from the literature [2, 10, 36]. The muffin-tin sphere radii used for Zn, Cd, Mg, V and O atoms are 2.0, 2.46, 1.39, 2.0 and 2.04 a.u., respectively. The k-point grid size of 2000 points in the whole Brillouin zone has been used here. For every calculation, convergence target of charge per cell was set below $10^{-4}$ electronic charge. In order to described the itinerant and localized behaviours of correlated electrons on equal footing, we have used the DFT+DMFT method as implemented in the study by Haule et al. [37]. DFT+DMFT calculations are carried out at room temperature, and are fully self-consistent in the electronic charge density and impurity levels. A continuous-time quantum Monte Carlo impurity solver has been used to solve the auxiliary impurity problem [38]. The exact DC scheme proposed by Haule has been used here [39], $t_{2g}$ orbitals are treated within DMFT. The density-density form of the Coulomb repulsion has been used in all calculations. The values of $U$ used here are taken from our earlier paper, in which the self-consistently calculated values of $U$ for ZnV$_2$O$_4$, CdV$_2$O$_4$ and MgV$_2$O$_4$ are 5.9, 5.7 and 6.2 eV, respectively [19]. Using these values of $U$, the Yukawa screening $\lambda$ (≈1.34, 1.38 and 1.28 a.u.$^{-1}$ for ZnV$_2$O$_4$, CdV$_2$O$_4$ and MgV$_2$O$_4$, respectively) was uniquely determined through the matrix elements of the Yukawa interaction in the DMFT basis. Similarly, the values of Hund’s coupling $J$ (≈1.0, 0.99 and 1.02 eV for ZnV$_2$O$_4$, CdV$_2$O$_4$ and MgV$_2$O$_4$, respectively) was uniquely determined by $\lambda$ through the Yukawa form of the Coulomb interaction [39]. Hence, all the parameters ($U$, $\lambda$ and $J$) used in the present study were material specific. The convergence of the charge/cell of these systems is set to be less than a $10^{-4}$ electronic charge. All these calculations are converged on the imaginary axis. Next, to obtain the self-energy on the real axis, we need to do an analytical continuation. The maximum entropy method is used for the analytical continuation of the self-energy from the imaginary frequency axis to real frequencies to obtain spectra on the real axis [40].

### Results and discussions.

The plots of the partial density of states (PDOS) of Zn 3d, Cd 4d, V 3d and O...
Electronic structure study of V spinels by using DFT and DMFT

Fig. 1: (Colour online) Partial density of states (PDOS) of (a) Zn 3d, V 3d and O 2p states for ZnV₂O₄, (b) Cd 4d, V 3d and O 2p states for CdV₂O₄ and (c) V 3d and O 2p states for the MgV₂O₄ compounds computed within DFT. For better comparison, PDOS of Zn 3d, Cd 4d, V 3d and O 2p states in regions III and IV is multiplied by a factor of seven (nine) for the ZnV₂O₄ (CdV₂O₄), while in region III, PDOS of V 3d and O 2p states in multiplied by a factor of five for the MgV₂O₄ compound. Zero energy corresponds to the Fermi level. Integrated background subtracted X-ray photoemission spectroscopy measurements data for ZnV₂O₄ and CdV₂O₄ are taken from ref. [41].

2p states of AV₂O₄ (A = Zn, Cd and Mg) compounds computed within DFT are shown in fig. 1(a)–(c). For both ZnV₂O₄ and CdV₂O₄, the plot of PDOS is divided into I, II, III, IV and V distinct regions, while it is divided into I, II, and III distinct regions for MgV₂O₄. For these compounds, the V 3d electronic character in the region I (above ~1 eV) of the conduction band (CB) is dominant, where they are more spread for CdV₂O₄ as compared to ZnV₂O₄ and MgV₂O₄. Also in this region, two strong peaks centered around ~2.4 eV and ~2.7 eV for CdV₂O₄ and one peak centered around ~2.7 eV for ZnV₂O₄ and MgV₂O₄ are observed. Similarly, the dominant electronic character in region II comes from the V 3d states, which are roughly extended from ~1.5 eV of the valence band (VB) to ~1 eV of CB for these compounds. In this region, V 3d states centered around the Fermi level are less broad for CdV₂O₄ as compared to ZnV₂O₄ and MgV₂O₄. In order to compare the PDOS below ~3 eV for these compounds, we have multiplied the PDOS for ZnV₂O₄, CdV₂O₄ and MgV₂O₄ by a factor of seven (~3 to ~7 eV), nine (~3 to ~8.5 eV) and five (below ~3 eV), respectively. Regions III and IV of VB are extended from ~3 to ~7 eV for ZnV₂O₄, where V 3d states are mixed with the Zn 3d and O 2p states. These states in regions III and IV are strongly peaked around ~4.5 eV and ~6 eV, respectively. The highest electronic character in regions III (IV) comes from the Zn 3d states (~47% (~52%)), while the lowest comes from V 3d states (~9% (~15%)). The regions III and IV of VB for CdV₂O₄ and region III of VB for MgV₂O₄ are extended from ~3 to ~8.5 eV and below ~3 eV, respectively, where V 3d states are mixed with Cd 4d and O 2p states for CdV₂O₄ and O 2p states for MgV₂O₄. These states are strongly peaked around ~4.6 eV and ~6.3 eV for CdV₂O₄ and ~5.7 eV for MgV₂O₄. Among these states, the contribution of the O 2p character ~61% (~53%) in regions III (IV) is highest, whereas the V 3d character ~10% (~21%) is lowest for CdV₂O₄. Similarly for MgV₂O₄, the dominant electronic character comes from O 2p states (~77%) in region III. In region V of VB, the dominating electronic character below ~7 eV comes from Zn 3d states of ZnV₂O₄ and below ~8.5 eV, Cd 4d states of CdV₂O₄. Now in order to compare our results with the experiment, we have also shown the x-ray photoemission spectroscopy measurements data (where the integrated background is subtracted from the experimental data) for ZnV₂O₄ and CdV₂O₄ in fig. 1(a) and (b) [41]. For MgV₂O₄, we could not find any experimental data available in the literature. It is also clear from the figure that the position of the theoretically predicted two peaks in regions III and IV for both compounds are located at ~0.6 eV higher energy than the experimentally observed peaks. Normally the theoretically predicted peak of the O 2p character within DFT is found close to the experiment as shown in the vanadium-based compounds [33].

In most of the transition metal oxides, the fivefold degenerate 3d orbitals in regular octahedral environment are split into lower energy threefold degenerate t₂g and higher-energy twofold degenerate e_g part, this is not the case here in vanadium spinels. Because of the presence of small trigonal distortion, the degenerate 3d orbitals of a V ion are split into non-degenerate 3z²−r², doubly degenerate x²−y² and xy (indicated by x²−y²+xy) and doubly degenerate xz and yz (indicated by xz+yz) orbitals. Here, in order to know the nature of the splitting of these orbitals, we have plotted orbitally resolved PDOS of a V atom for these compounds in fig. 2(a)–(c). For a better comparison, we have multiplied the PDOS of these orbitals by a factor of seven below ~2 eV for these compounds. The plot of PDOS is divided into I, II and III distinct regions. Above ~1 eV, almost negligible contribution comes to PDOS from the 3z²−r² orbital for these compounds in region I of CB. In this region, the behaviour of the x²−y²+xy and xz+yz orbitals is almost the same for these compounds. These orbitals are sharply peaked around ~2.3 eV and ~2.6 eV for CdV₂O₄ and ~2.6 eV for ZnV₂O₄ and MgV₂O₄. The x²−y²+xy and xz+yz orbitals are less extended for MgV₂O₄ as compared to other two compounds. In region II (~2 to ~1 eV) of VB and CB, there is a finite weight of all these orbitals around
the Fermi level for these spinels, where among these orbitals the largest peak of the $3z^2 - r^2$ orbital is observed at the Fermi level. However, the $x^2 - y^2 + xy$ and $xz + yz$ orbitals are sharply peaked as compared to the $3z^2 - r^2$ orbital around $\sim 0.5$ eV for CdV$_2$O$_4$ and $\sim 0.7$ eV for ZnV$_2$O$_4$ and MgV$_2$O$_4$. Around these energies, almost equal contributions from the $x^2 - y^2 + xy$ and $xz + yz$ orbitals are observed for these spinels. The regions I and II are identified as anti-bonding V 3d orbitals, where the energy of the $x^2 - y^2 + xy$ orbitals is lowest and that of the $xz + yz$ orbitals is largest as compared to that of the $3z^2 - r^2$ orbital for these spinels. In region III (below $\sim -2$ eV) of VB, V 3d orbitals are extended in the largest energy range for CdV$_2$O$_4$ and in the smallest for MgV$_2$O$_4$ as compared to ZnV$_2$O$_4$. In this region, as compared to other orbitals the contribution from the $3z^2 - r^2$ orbital is very small compared to the PDOS. The $xz + yz$ orbitals are strongly mixed with the $x^2 - y^2 + xy$ orbitals around $\sim -5.7$ eV for these spinels. Also, in this region, the $xz + yz$ orbitals are sharply peaked around $\sim -4.5$ eV and $\sim -8.0$ eV for ZnV$_2$O$_4$, $\sim -4.5$ eV and $\sim -6.4$ eV for CdV$_2$O$_4$ and $\sim -6.4$ eV for MgV$_2$O$_4$, where the contributions to PDOS from other orbitals are very small. This region is attributed to the bonding V 3d orbitals, where the energy of the $3z^2 - r^2$ orbital is lowest and that of the $x^2 - y^2 + xy$ orbitals is largest as compared to that of the $xz + yz$ orbitals. The electron occupancy of $3z^2 - r^2$ and $xz + yz$ orbitals changes slightly from $\sim 0.65$ to $\sim 0.71$ (1.11) to $\sim 0.66$ to $\sim 0.67$ (1.13) to $\sim 0.64$ to $\sim 0.70$ (1.12) as the compound changes from ZnV$_2$O$_4$ to CdV$_2$O$_4$ to MgV$_2$O$_4$.

In fig. 3(a)–(c), we have plotted the total densities of states (TDOS) calculated in the DFT+DMFT approach. In order to compare the TDOS with the experimental data (where the total energy resolution was $\sim 0.6$ eV), we have included the instrument broadening (IB) of 0.6 eV for these spinels. The TDOS computed by including IB are also shown in fig. 3. It is clear from the figure that an incoherent shoulder (the so-called lower Hubbard band) appears at $\sim -0.9$ eV, $\sim -1.1$ eV and $\sim -1.0$ eV for ZnV$_2$O$_4$, CdV$_2$O$_4$ and MgV$_2$O$_4$, respectively, which are slightly mismatched from the experimental data. However, by including the IB to TDOS of these compounds, the position of the lower Hubbard band is shifted by $\sim 0.15$ eV towards the lower energy side, which is in good agreement with the experimental data for ZnV$_2$O$_4$. However, it is still $\sim 0.2$ eV mismatched from the experimental data for CdV$_2$O$_4$. The behaviour of the calculated TDOS is in good agreement with the experiment from the Fermi level to $\sim -4.5$ eV for both compounds. However, below $\sim -4.5$ eV, the position of the two peaks is not matched with the experimental data, where similarly to DFT data both peaks are located at a $\sim 0.6$ eV higher energy with respect to experimental results. Now in order to match the position of the lower Hubbard band with the experimental data for CdV$_2$O$_4$, we have increased the values of $U$. For $U = 8$ eV and $J = 1.1$ eV, the position of the lower Hubbard band is matched with the experimental
data as also shown in fig. 3. The slight mismatching of the theoretically calculated lower Hubbard band with the experimental data corresponding to self-consistent calculated parameters for CdV$_2$O$_4$ may be due to some other reasons, for which careful study is needed in this direction.

The plot of PDOS of Zn 3d, Cd 4d, V 3d and O 2p states and O 2p states of these spinels computed within the DFT+DMFT approach are shown in fig. 4(a)–(f). For ZnV$_2$O$_4$, the plots of PDOS of Zn 3d, V 3d and O 2p states are divided into three distinct regions, I (above the Fermi level), II (Fermi level to ~ -7 eV) and III (below ~ -7 eV). Similarly, the plots of PDOS of Cd 4d, V 3d and O 2p states of CdV$_2$O$_4$ are also divided into three distinct regions, I (above the Fermi level), II (Fermi level to ~ -8.5 eV) and III (below ~ -8.5 eV). While it is divided into two distinct regions, I (above the Fermi level) and II (below the Fermi level) for MgV$_2$O$_4$. Now, in order to compare the PDOS for these states, we have multiplied the PDOS of region II by a factor of four for these compounds. It is clear from fig. 4 that the quasiparticle peaks of the V 3d character cross the Fermi level within DFT and are disappeared in the DFT+DMFT calculations. Hence, the band gap ($E_g$) is created for these vanadates. We will discuss the $E_g$ for these compounds in the later part of the manuscript in more detail. In regions I and II, two sharp peaks of dominant V 3d character for ZnV$_2$O$_4$ (CdV$_2$O$_4$) are found to be around ~3 eV (~2.7 eV) and ~ -0.9 eV (~ -1.1 eV). Similarly, they are found to be around ~2.9 eV (region I) and ~ -1 eV (region II) for the MgV$_2$O$_4$ compound. In region II, Zn 3d, Cd 4d and O 2p states are observed below ~ -3 eV for these spinels, where they are strongly mixed with V 3d states. The position of the sharp peaks observed here are not shifted appreciably from the DFT results for these compounds. In region III, below ~ -7 eV for ZnV$_2$O$_4$ and below ~ -8.5 eV for CdV$_2$O$_4$, the dominant electron character comes from Zn 3d and Cd 4d states, respectively. The position of these states for both compounds are also not shifted appreciably from the DFT calculations.

The plots of PDOS of the xy and xx/yz orbitals are also shown in fig. 4, where they are divided into two distinct regions, I (above the Fermi level) and II (below the Fermi level). In region I of CB, the incoherent shoulders of these orbitals are observed around ~2 eV for these compounds. In this region, among these orbitals, the large electronic character comes from the xy orbital for ZnV$_2$O$_4$ and CdV$_2$O$_4$, while it comes from the xx/yz orbitals for MgV$_2$O$_4$. The energy of the xy orbital is lower than that of the xx/yz orbitals for ZnV$_2$O$_4$ and CdV$_2$O$_4$. However, for MgV$_2$O$_4$, the energy of the xx/yz orbitals is found to be lower than that of the xy orbital. In region II of VB, all three orbitals are sharply peaked around ~ -0.9 eV, ~ -1.1 eV and ~ -1 eV for ZnV$_2$O$_4$, CdV$_2$O$_4$ and MgV$_2$O$_4$, respectively. In this region, the opposite behaviour of these orbitals is observed as the compared to the region I. The partial occupancy of the xy orbital increases slightly from ~0.63 to ~0.65 to ~0.69 as the compound changes from ZnV$_2$O$_4$ to CdV$_2$O$_4$ to MgV$_2$O$_4$, while the partial occupancy of the xx/yz orbitals decreases slightly from ~0.69 to ~0.68 to ~0.66 as the compound changes from ZnV$_2$O$_4$ to CdV$_2$O$_4$ to MgV$_2$O$_4$. However, the total occupancy of the $t_{2g}$ orbitals is ~2.01 for these spinels. The occupancy of the xy, xx/yz and $t_{2g}$ orbitals is about 1.2, 2 and 1.6 times larger than DFT results, respectively. The different orbital occupancy of these orbitals from compound to compound in both approaches is due to the different V-O and V-V bonds and V-O-V angles in the trigonal distorted VO$_6$ octahedra for these spinels. Different bonds and angles influence the orbital occupancy and they are due to the different ionic radii of Zn, Cd and Mg ions in these compounds.

The calculated values of $E_g$ for ZnV$_2$O$_4$, CdV$_2$O$_4$ and MgV$_2$O$_4$ are ~0.9 eV, ~0.95 eV and ~1.15 eV, respectively. For ZnV$_2$O$_4$ and MgV$_2$O$_4$ compounds, the values of $E_g$ computed in the present study are about three times larger than the experimental data reported by Rogers et al. However, the experimentally observed
values of $E_g$ by Pardo et al. are $\sim 1.1 \text{eV}$, $\sim 1.08 \text{eV}$ and $\sim 3.16 \text{eV}$ for the ZnV$_2$O$_4$, MgV$_2$O$_4$ and CdV$_2$O$_4$, respectively. The calculated values of $E_g$ are close to the experimental values for the ZnV$_2$O$_4$ and MgV$_2$O$_4$ compounds. However, they are about three times smaller than the experimental data for CdV$_2$O$_4$. As mentioned above for $U = 8 \text{eV}$ and $J = 1.1 \text{eV}$, the position of the lower Hubbard band matches the experimental result for the CdV$_2$O$_4$ compound. Correspondingly to these parameters, the DFT+DMFT approach still underestimates the value of $E_g$ ($\sim 1.6 \text{eV}$) as, compared to the experimental result ($\sim 3.16 \text{eV}$) for this compound. Experimentally, the value of $E_g$ depends on the activation energy for the resistivity, which itself depends on whether the spinel sample is made in pure phase or not. However, it is always a challenging task to make the spinel sample in pure phase. In the light of these facts, it is difficult to compare the theoretically computed and experimentally observed values of $E_g$ for these compounds. For these parameters, the values of $E_g$ computed in the present study for these compounds are reasonable as, corresponding to these parameters, our data are closely matched with the experiment in VB. Here, it will be interesting to see whether the inverse photoemission spectroscopy measurements data will be helpful to explain our results in CB for these compounds.

It is well known that in insulating vanadium spinels, the localization of V 3$d$ electrons is not in the fully localized limit. Based on the localized-electron superexchange represented by $J \propto \frac{t}{U}$ (where $t$ is the transfer integral between neighbouring sites), Canosa et al. have argued qualitatively the order of the degree of localization of these electrons for CdV$_2$O$_4$ > ZnV$_2$O$_4$ > MgV$_2$O$_4$ [18]. However, based on the calculated values of the ratio between the average values of the nearest neighbour $t$ and the self-consistently computed values of $U$ in our earlier work, we have shown that the degree of localization of these electrons decreases from CdV$_2$O$_4$ to MgV$_2$O$_4$ to ZnV$_2$O$_4$ [19]. In that study, the average values of $t$ for these spinels were computed indirectly by fitting the following equation [42]:

$$J \approx \frac{4t^2}{U}$$

valid to the localized limit. $J$ was the average nearest-neighbour exchange coupling constant. Here, based on the impurity hybridization function (which gives the direct information about the degree of localization of correlated electrons), it is interesting to see the order of the degree of localization of V 3$d$ electrons in these spinels. Hence, we have computed the average impurity hybridization function (average over all $t_{2g}$ orbitals of the V site) for these compounds, which is shown in fig. 5. Below the Fermi level, the average impurity hybridization function is sharply peaked around $\sim -1 \text{eV}$, $\sim -1.1 \text{eV}$ and $\sim -1.15 \text{eV}$ for ZnV$_2$O$_4$, MgV$_2$O$_4$ and CdV$_2$O$_4$, respectively. Around these energies, it is largest for ZnV$_2$O$_4$ and smallest for CdV$_2$O$_4$ as compared to MgV$_2$O$_4$. A large value of the average impurity hybridization function indicates the less localized electronic character for the system. Hence, the degree of localization of the V 3$d$ electrons decreases from CdV$_2$O$_4$ to MgV$_2$O$_4$ to ZnV$_2$O$_4$, which is consistent with our earlier results based on the above discussed $\frac{t}{U}$ ratio.

Conclusions. – In conclusion, the exact comparative behaviour of various physical properties of AV$_2$O$_4$ (A = Zn, Cd and Mg) compounds has not been found, where material-specific parameters were used. In the present work, we have explored the comparative behaviour of electronic structures of these compounds by using the DFT+DMFT approach, where material-specific parameters were used. The calculated order of $E_g$ was found to be MgV$_2$O$_4$ ($\sim 1.15 \text{eV}$)> CdV$_2$O$_4$ ($\sim 0.95 \text{eV}$)> ZnV$_2$O$_4$ ($\sim 0.9 \text{eV}$), where the values of $E_g$ were close to the experimental data for ZnV$_2$O$_4$ and MgV$_2$O$_4$. Among these spinels, the average impurity hybridization function of the V site was found to be largest for ZnV$_2$O$_4$ and smallest for CdV$_2$O$_4$. Hence, the degree of localization of V 3$d$ electrons was highest for CdV$_2$O$_4$ and lowest for ZnV$_2$O$_4$ as compared to the MgV$_2$O$_4$ compound. This order of the degree of localization of V 3$d$ electrons was found to be consistent with our earlier results. In the energy range from 0 to $\sim -4.5 \text{eV}$, an almost a similar behaviour of the calculated total density of states and experimental data was observed for these spinels, where the position of the lower Hubbard band was in good agreement with the experiment for ZnV$_2$O$_4$.

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