Systematic analysis of structural and magnetic properties of spinel CoB$_2$O$_4$ (B = Cr, Mn and Fe) compounds from their electronic structures

Debashish Das, Rajkumar Biswas and Subhradip Ghosh

Department of Physics, Indian Institute of Technology Guwahati, Guwahati, Assam 781039, India

E-mail: subhra@iitg.ernet.in

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Abstract

The structural and magnetic properties of spinel compounds CoB$_2$O$_4$ (B = Cr, Mn and Fe) are studied using the DFT+U method and generalized gradient approximation. We concentrate on understanding the trends in the properties of these materials as the B cation changes, in terms of relative strengths of crystal fields and exchange fields through an analysis of their electronic densities of states. We find that the electron–electron correlation plays a significant role in obtaining the correct structural and electronic ground states. Significant structural distortion in CoMn$_2$O$_4$ and ‘inverted’ sublattice occupancy in CoFe$_2$O$_4$ affects the magnetic exchange interactions substantially. The trends in the magnetic exchange interactions are analysed in terms of the structural parameters and the features in their electronic structures. We find that the Fe states in CoFe$_2$O$_4$ are extremely localised, irrespective of the symmetry of the site, which makes it very different from the features of the states of the B cations in two other compounds. These results provide useful insights into the trends in the properties of CoB$_2$O$_4$ compounds with variation of B cation, which would help in understanding the results of recent experiments on doping of Mn and Fe in multiferroic CoCr$_2$O$_4$.

Keywords: spinel, magnetism, oxide, density functional theory, exchange interactions, electronic structure

(Some figures may appear in colour only in the online journal)
The A, B and oxygen atoms are shaded in green, purple and red, respectively.

These results imply that the substitution of Cr by another magnetic atom renormalises the intra- and inter-sublattice magnetic interactions and can be directly connected to the novel magnetism related phenomena. However, in order to understand the basic physics of such complex phenomena and interpret the experimental observations, one needs to have a clearer understanding at the microscopic level. Such understanding can be achieved if the end compounds, that is CoCr2O4, CoMn2O4 and CoFe2O4, are investigated in a systematic manner and various physical properties of these materials are understood at a microscopic level, that is, from their electronic structures.

The standardised parameter-free approach to calculate the electronic structures and the physical properties is the various implementations of the density functional theory (DFT) [14]. There is no systematic exploration of the compounds under consideration here using DFT based electronic structure methods. There have been very few DFT based calculations of CoCr2O4 [15, 16] and of CoFe2O4 [17–19] only. These calculations provided important insights into the interrelations of sub-lattice occupancies, structural properties and magnetic properties of these materials on the basis of their electronic structures.

In this communication, we present a systematic study of the three compounds CoB2O4 (B = Cr, Mn, Fe) with the focus on understanding the similarities and differences in their electronic structures, and thus the structural and magnetic properties in particular. We do this using DFT based calculations. Detailed information on the structural parameters, their influences on the electronic structures, the variations in the crystal fields and exchange fields and their effects on the magnetic properties as one changes the B element are provided. These results serve as important prerequisites to analyse the systems when they are doped with a third magnetic atom. The paper is organised as follows: section 2 details the computational tools used, section 3 provides and analyses the results, followed by the conclusions.

2. Computational details

We have used the DFT+U [20] method for all our calculations in order to address the electron–electron strong correlation effects that are necessary for oxide systems. Among various different adoptions of DFT+U, we have used the approach of Dudarev et al [21] where the effects of on-site Coulomb correlation and Hund’s coupling are represented through an effective parameter $U_{\text{eff}} = U - J$, $U$ being the strength of the Coulomb interaction and $J$ the Hund’s coupling. In our calculations, $J$ has been kept at 1 eV as previous DFT calculations for a number of transition metal oxides showed that $J$ remains nearly constant for the entire transition metal series [22]. The coulomb parameter $U$ has been taken to be 3 eV for Cr, 4 eV for Mn and Fe, 5 eV for Co. The rationale behind such choices have been explained earlier [16]. The self-consistent quantum mechanical equations are solved using the projector augmented wave (PAW) [23] basis set as implemented in the VASP code [24]. The exchange correlation part of the Hamiltonian was treated with the PBE—generalized gradient approximation (GGA) [25] functional. A plane wave cut off of 550 eV and 5 5 5 Å k-point for Brillouin zone integrations have been used throughout to ensure an energy convergence of 10$^{-7}$ eV. For structural relaxations the convergence criteria of force on each atom was set at 10$^{-4}$ eV Å$^{-1}$.

3. Results and discussions

3.1. Modeling of the sub-lattice occupancy and spin configuration

The spinel structure belongs to cubic space group $Fd\bar{3}m$ with two types of cation sublattice-A and B. The A sublattice has tetrahedral symmetry and is usually occupied by a cation in the +2 state. The B sublattice has octahedral symmetry and is usually occupied by a cation in the +3 state (figure 1). One formula unit of the spinel consists of one A sublattice and two B sublattices. In the case of one B atom occupying the tetrahedral positions by displacing the A atom to the octahedral sites, the structure is known as ‘Inverse spinel’. Among the three compounds under consideration, the CoCr2O4 is found to be crystallising in ‘Normal spinel’ structures [26]. In the case of CoMn2O4, although the sub-lattice occupancy conforms to that of spinel, the crystal structure is tetragonal with space group $I41/amd$ [27]. CoFe2O4, on the other hand, has no structural distortion, but has the sub-lattice occupancy alike Inverse spinel [28]. The sub-lattice occupancies in CoFe2O4 are found out to be crucial in determining whether the ground state is insulator or half-metal [17, 18]. Regarding the ground state magnetic structure, neutron diffraction studies have shown

Table 1. The lattice parameters of CoB2O4.

| Structural parameter | CoCr2O4 | CoMn2O4 | CoFe2O4 |
|----------------------|---------|---------|---------|
| $a$ (Å)              | 8.35(8.34)$a$ | 8.17(8.1$b$) | 8.41(8.366)$b$ |
| $b$ (Å)              | 8.35(8.34)$a$ | 8.17(8.1$b$) | 8.41(8.366)$b$ |
| $c$ (Å)              | 8.35(8.34)$c$ | 9.39(9.13$d$,$0.3$) | 8.45(8.366)$c$ |
| $x$                  | 0.262(0.26$4 ^{d}$) | 0.255(0.23$d$) | 0.255(0.256$b$) |
| $y$                  | 0.262(0.26$4 ^{d}$) | 0.255(0.23$d$) | 0.255(0.256$b$) |
| $z$                  | 0.262(0.26$4 ^{d}$) | 0.267(0.256$d$) | 0.255(0.256$b$) |

$^{a}$ Wickham and Croft [30]. $^{b}$Boucher et al [27]. $^{c}$Wickham and Croft[31]. $^{d}$Teillet et al [28].

Note: $a$, $b$, $c$ are the lattice constants. $x$, $y$, $z$ are the oxygen parameters.


that CoCr$_2$O$_4$ and CoMn$_2$O$_4$ have canted spin structures [7, 27] while CoFe$_2$O$_4$ has a ferrimagnetic collinear structure, with the moments at A and B sites anti-aligning, giving rise to the Neel configuration [28]. Mossbauer studies [29] later confirmed this.

The sub-lattice occupancy for CoCr$_2$O$_4$ and CoMn$_2$O$_4$ have been taken to be like normal spinels as has been found from experiments. For CoFe$_2$O$_4$, inverse spinel sub-lattice occupancy with maximum inversion has been considered. In absence of disorder at a particular sub-lattice, this configuration is found to have the lowest energy [18]. Since modeling of the sub-lattice disorder requires either construction of a supercell in the present approach or consideration of a mean field configuration averaging procedure [19], we have considered the complete inverse spinel type sub-lattice occupancy. Since the motivation behind this work is a systematic understanding of the three systems as the chemical identity of the B atom changes, we have taken the magnetic configurations of the three systems to be collinear. Although CoCr$_2$O$_4$ and CoMn$_2$O$_4$ have non-collinear magnetic ground states, the investigations into the collinear magnetic states would provide important qualitative insights. In order to find out the relative alignments of the spins at various sub-lattices, we have taken two formula units of the unit cell and done total energy calculations on different collinear spin configurations. We found the Neel configuration to be energetically lowest in the case of CoCr$_2$O$_4$ and CoFe$_2$O$_4$. In the case of CoMn$_2$O$_4$, we found a magnetic configuration in which the spins at the sites of a given sub-lattice are anti-parallel, giving rise to a zero magnetic moment at each sub-lattice, lowest in energy. However, the energy of the Neel configuration is higher by about only 1 meV per atom. This result indicates that the actual magnetic ground state of CoMn$_2$O$_4$ would be frustrated. In subsequent analysis we have therefore considered only the Neel configuration.

### 3.2. Structural parameters

The lattice parameters obtained after full structural relaxations using DFT+U for the three compounds are given in table 1. Figure 2 provides the details of various bond lengths and bond angles, thus providing a close-up view of the structures around the tetrahedral and the octahedral sites. The lattice parameters agree well with the available experimental results. CoCr$_2$O$_4$ stabilises in the cubic structure with almost no local distortion at the tetrahedral site as can be seen from the ideal spinel value of $109.47^\circ$ for the O–Co–O angle. There is slight local distortion at the octahedral site; the O–Cr–O bond angle is $84.55^\circ$, deviating from the ideal value of $90^\circ$ and the Co–O–Cr bond angle is $121.53^\circ$ in place of the ideal value of $125^\circ$. CoMn$_2$O$_4$, on the other hand, has a tetragonal crystal structure with $c/a = 1.16$. Subsequently various bond distances and bond angles, (figure 2(b)), are significantly dispersed. One can now see substantial distortion associated with the tetrahedral sites as the O–Co–O bond angles are
108.14° ± 4.13°. The octahedra too distorts considerably with elongation (contraction) of Mn–O bonds along z(xy) directions, (figure 2(b)). This leads to significant variations in the O–Mn–O and Mn–O–Co angles. The differences in the distortions in the octahedra around the B sites in CoMn2O4 in comparison to CoCr2O4 is pictorially represented in figure 3. In the case of CoFe2O4, our calculations produce a slight departure from the perfect cubic structure, the c-axis elongated by about 0.5%. This slight loss of cubic symmetry is due to different distortions of the octahedra around Co and Fe sites. Figure 3(c) shows that while there is slight elongations of Co–O bonds along the z-direction, the Fe–O bonds in the same direction contract in comparison with the same bonds in the xy planes. This gives rise to the small tetragonality. The bond angles, (figure 2(c)), associated with the octahedral and tetrahedral sites clearly show that the distortions are associated with Co atoms in the octahedral sites. The O–Co–O bond angle deviates to 88.23° ± 2° as opposed to the O–Fe–O bond angle of 90.24° ± 0.07° which is quite close to the ideal spinel value of 90°. Similarly, the FeCr1–O–Feγ bond angle is 124.16°, while that of the CoO–O–Feγ bond angle is 121.53°, a larger deviation from the ideal spinel value of 125°.

The energy level diagrams based upon the electronic configurations of the cations occupying the tetrahedral and octahedral sites can explain the observed trends in the structural aspects of the CoB2O4 compounds considered here. Figure 4 shows that in the case of CoCr2O4, the higher lying eg states of octahedral Cr3+ are empty while the t2g configuration of Mn3+ in CoMn2O4 implies degeneracy associated with this level. In order to lift the degeneracy, the symmetry of the crystal structure is lowered, giving rise to the tetragonal ground state. The largeness in the tetragonal distortion can be understood from the (t2g)5(eg)2 configuration of the Mn3+ ions as explained by Dunitz and Orgel [32]. In the case of CoFe2O4, the degeneracy associated with the t2g orbitals of the Co2+ ions leads to the lowering of the cubic symmetry. The small value of the distortion can once again be understood from the (t2g)5(eg)2 of the Co atom in the octahedral site [32].

3.3. Electronic structure and magnetic moments

The configurations of d electrons at different cation sites play the most important role in determining the electronic and magnetic properties of spinel oxides. According to crystal field theory [33], the electronic configuration depends on the relative strengths of the crystal field (CF) and intra-atomic exchange field (EX). In this section, we attempt an understanding of the relation between the structural distortions and electronic structures in CoB2O4 compounds by investigating the relative strengths of crystal field splitting and exchange splitting through an analysis of the densities of states. Consequently, this would lead to the understanding of the electronic and magnetic properties of these systems.

The schematic representation of electrons in d levels in figure 4, based upon crystal field theory, shows that in a tetrahedral crystal field, the eg levels lie lower than the t2g levels due to direct electrostatic repulsion between the t2g orbitals and the surrounding anion orbitals, while in an octahedral crystal field, the order is reversed as the eg orbitals are repelled in this case. Upon tetragonal distortion, the eg levels associated with the octahedral sites further split into two levels with the dxy,dyz, and dz2 orbitals at a energy higher than dxz, and the dx2−xy level splits into a higher dx2 level and a lower doubly degenerate dz2,dyz level when c/a > 1. The spacings of these energy levels depend on the strengths of the crystal fields and the exchange fields.

In table 2 we present results for crystal field splitting (ΔCF) and the exchange splitting (ΔEX) for the three compounds. These results are obtained without incorporation of correlations that is by setting Ueff = 0. A comparison of results for the three show that the stronger exchange splitting associated with the t2g states, in comparison to crystal field splitting, is a common feature for the compounds. This should lead to high spin states for both magnetic cations. The results suggest that for all three materials, the five-fold 3d crystal degeneracy is barely broken for the down spin (↓) channel of A site. Therefore, irrespective of the chemical identity of the species at A site, this spin band is nearly full. For CoCr2O4 and CoMn2O4, the other 3d electrons mostly occupy the exchange split (ΔEX = 1.6 eV) eg up spin (↑) channel. In the case of CoFe2O4, the exchange splitting of eg levels is double that of the other two compounds. This is due to the fact that in CoFe2O4, the Fe3+ occupies the

\[ \text{Figure 4. Electronic configurations for cations occupying A and B sites in CoB2O4 compounds. (a) CoCr2O4. (b) CoMn2O4. (c) CoFe2O4.} \]
tetrahedral sites having two electrons less than Co$^{2+}$, which occupies tetrahedral sites in the other two compounds, making the $e_g$ states nearly empty. The $t_{2g}$ states in all cases are energetically higher and thus remain mostly unoccupied (not shown here), the exchange splitting associated with $t_{2g}$ states ($\Delta_{t_{2g}}^{\text{EX}}$) being nearly constant, therefore.

The large exchange splitting of the $t_{2g}$ states at the B site for CoCr$_2$O$_4$ and CoMn$_2$O$_4$ indicate that one of the spin bands is nearly full and the other nearly empty. This indeed is the case with the $t_{2g}$ bands are nearly full in both cases (not shown here). For CoFe$_2$O$_4$, there are two different values of $\Delta_{t_{2g}}^{\text{EX}}$ corresponding to Fe$^{2+}$ and Co$^{2+}$. While the exchange splitting for Fe is nearly the same as that of Cr and Mn, it is smaller for Co. The reason is that Co$^{2+}$ has two more electrons than Cr (Mn, Fe) and hence part of the down ($\downarrow$) spin channel is also occupied. The exchange splitting of $e_g$ states at the B site for CoCr$_2$O$_4$ and CoMn$_2$O$_4$ are much smaller as the $e_g$ band is nearly empty for both spins. One extra electron in the $e_g$ band of CoMn$_2$O$_4$ in comparison to CoCr$_2$O$_4$ increases $\Delta_{e_g}^{\text{EX}}$ for the former. In the case of CoFe$_2$O$_4$, $\Delta_{t_{2g}}^{\text{EX}}$ are comparable for both Co and Fe at the B site. This is expected as both Co$^{2+}$ and Fe$^{3+}$ have one spin channel completely full and the other completely empty. The extra electron in Mn$^{3+}$ $e_g$ band (as compared to Cr$^{3+}$ and Mn$^{3+}$) explains the reason behind smaller values of crystal field splitting (for both bands) in CoMn$_2$O$_4$ than in CoCr$_2$O$_4$.

In CoFe$_2$O$_4$, $\Delta_{t_{2g}}^{\text{CF}}$ for both Co$^{2+}$ and Fe$^{3+}$ are the largest while $\Delta_{e_g}^{\text{CF}}$ are smaller than that for Cr$^{3+}$ and Mn$^{3+}$ in the other two compounds. The smaller values of $\Delta_{e_g}^{\text{CF}}$ are due to the fact that for both cations, up($\uparrow$) bands are nearly full and therefore, the centers of $t_{2g}$ and $e_g$ bands lie much closer than those of Cr$^{3+}$ and Mn$^{3+}$ in the other two compounds. The largest crystal field splittings for up($\uparrow$) bands of Co$^{2+}$ and Fe$^{3+}$ in CoFe$_2$O$_4$ are due to the fact that unlike Cr$^{3+}$ and Mn$^{3+}$ in other two compounds, the $t_{2g}$ are not completely empty. Thus, the separation between $t_{2g}$ and $e_g$ bands are larger compared to the other two. The

| System    | Ion     | $\Delta_{e_g}^{\text{EX}}$ | $\Delta_{t_{2g}}^{\text{EX}}$ | $\Delta_{t_{2g}}^{\text{CF}}$ | $\Delta_{e_g}^{\text{CF}}$ | Ion     | $\Delta_{e_g}^{\text{EX}}$ | $\Delta_{t_{2g}}^{\text{EX}}$ | $\Delta_{t_{2g}}^{\text{CF}}$ | $\Delta_{e_g}^{\text{CF}}$ |
|-----------|---------|---------------------------|-------------------------------|-------------------------------|---------------------------|---------|---------------------------|-------------------------------|-------------------------------|---------------------------|
| CoCr$_2$O$_4$ | Co$^{2+}$ | 1.6                       | 2.9                           | 0.0                           | 1.3                       | Cr$^{3+}$ | 1.3                       | 3.2                           | 1.3                           | 3.3                       |
| CoMn$_2$O$_4$ | Co$^{2+}$ | 1.6                       | 2.5                           | 0.5                           | 1.3                       | Mn$^{3+}$ | 1.8                       | 3.7                           | 0.3                           | 2.2                       |
| CoFe$_2$O$_4$ | Fe$^{3+}$ | 3.3                       | 3.1                           | 1.0                           | 0.8                       | Fe$^{3+}$ | 3.5                       | 3.7                           | 1.7                           | 1.9                       |

Table 2. Exchange splitting ($\Delta_{\text{EX}}$) and crystal field splitting ($\Delta_{\text{CF}}$) results for the three compounds.
outcome of the competition between the crystal field splitting and the exchange splitting would affect the semiconducting band gap in these materials. In the case of CoCr$_2$O$_4$, equally strong exchange splitting and crystal field splitting at Cr site decides the gap. For the other two compounds, weaker crystal field splitting compared to the exchange splitting at B sites should result in a decrease in the band gap as the B occupation changes from Cr to Mn and Fe. However, with the GGA only calculations, ground states of CoMn$_2$O$_4$ and CoFe$_2$O$_4$ are metallic. This is because of the presence of finite densities of $t^2_g$ states at the Fermi level of B site atoms (not shown here). This can be correlated to the fact that without the inclusion of strong correlations, CoMn$_2$O$_4$ crystallizes in a cubic structure, thus unable to obtain the symmetry breaking of the $d$ orbitals and distribution of states on both sides of the Fermi level. In the case of CoFe$_2$O$_4$, the distortion at the Co site is small and thus the local symmetry is barely broken, resulting in the localisation of states at the Fermi level. The inclusion of electron–electron correlation through GGA+U formalism produces the correct semiconducting ground states by breaking the degeneracies in the $e_g$ orbitals of Mn cations in CoMn$_2$O$_4$. The total and atom projected densities of states calculated with GGA+U are presented in figures 5–7. In CoCr$_2$O$_4$, Co $t^2_g$ electrons are localised around $-6$ eV and $e^1_g$ states are localised around $-2$ eV. In the down spin (↓) band, it is the $e^1_g$ states that primarily hybridise with the oxygen $p$ states. The $t^2_g$ Co states are unoccupied and centred around $2$–$4$ eV, while the $2$ $e^1_g$ electrons are localised between $-1$ eV and $-2$ eV in the up (↑) spin channel. This gives rise to a magnetic moment of about $3$ $\mu_B$ at the Co site (table 3). At the Cr site, the incorporation of strong correlation does not have a very significant effect on the $t^2_g$ states, the $t^1_g$ states are still fully occupied with the electrons localised near the Fermi level while the fully unoccupied $t^3_g$ states are pushed towards higher energies. The $t^2_g$ states thus weakly hybridise with the oxygen states. The $e_g$ band is nearly empty as it was when calculations were done without incorporating $U_{eff}$. This results in a magnetic moment of nearly $3$ $\mu_B$ for Cr atoms as well, with the sign of the moment opposite to that of Co atoms, (table 3).

In CoMn$_2$O$_4$, (figure 6), the $t^2_g$ states of Co are qualitatively similar to those in CoCr$_2$O$_4$, except that they are shifted as a whole towards lower energy. The $e^1_g$ states at the Co site are more delocalised in comparison to those in CoCr$_2$O$_4$, leading to more hybridisation between Co $e^1_g$ and oxygen $p$ states. This, however, still gives rise to a magnetic moment of nearly $3$ $\mu_B$ for Cr atoms as well, with the sign of the moment opposite to that of Co atoms, (table 3).

In CoMn$_2$O$_4$, the $t^2_g$ states of Co are qualitatively similar to those in CoCr$_2$O$_4$, except that they are shifted as a whole towards lower energy. The $e_g$ states at the Co site are more delocalised in comparison to those in CoCr$_2$O$_4$, leading to more hybridisation between Co $e^1_g$ and oxygen $p$ states. This, however, still gives rise to a magnetic moment of about $3\mu_B$ at the Co site, like CoCr$_2$O$_4$. The densities of states at the Mn site are more interesting as the degeneracy of the $d$ states are lifted due to large tetragonal distortion. According to crystal field theory, the higher energy $e^1_g$ states should split into $d_{x^2-y^2}$ and $d_{z^2}$ states with $d_{x^2}$ being occupied and $d_{z^2}$–$y^2$ participating in covalent bond formation with oxygen [34]. In figure 6 (bottom panel), we indeed see this happening. The half-filled $d^2_{z^2}$ gives rise to distinct peaks at around $-6$ eV and at around $1$ eV. The $d_{x^2-y^2}$ states are more delocalised, having participated in hybridisations with oxygen $p$ states. The down

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**Figure 6.** The total (top panel) and site projected densities of states (A in the middle and B in the bottom panel along with anion contributions) for CoMn$_2$O$_4$. The energies are plotted with respect to Fermi level.
spin channel is nearly empty, leading to a Mn moment of nearly 4 \( \mu_B \) (table 3). The lifting of degeneracy has less effect on the \( t_{2g} \) states except that they are more delocalised in comparison to the case when the effect of electron–electron correlation was absent and the crystal structure was cubic. Overall, the extra electron in the \( e_g \) band of Mn (in comparison to Cr) gives rise to states closer to the Fermi level and thus reduces the electronic band gap in CoMn\(_2\)O\(_4\) in comparison to the band gap in CoCr\(_2\)O\(_4\) as expected. The calculated band gap in CoCr\(_2\)O\(_4\) is 2.1 eV while that of CoMn\(_2\)O\(_4\) is 0.33 eV.

In CoFe\(_2\)O\(_4\), different sub-lattice occupancy due to the ‘inverted’ structure introduces qualitative differences of both A and B sites densities of states, (figure 7). The introduction of strong correlations pushes the unoccupied states in the spin up band towards higher energy. The completely filled spin down band has electrons extremely localised around \(-6\) eV to \(-7\) eV allowing little hybridisations with the oxygen states. This leads to a moment of 4 \( \mu_B \) for Fe\(_T\) atoms. At the octahedral site, there are two types of atoms, Fe\(_O\) and Co. We see qualitatively very different features of the states associated with these two atoms. The \( e_g \) band is completely empty for either atoms. For Fe\(_O\), the \( t_{2g} \) band is completely full and is extremely localised around \(-6\) eV to \(-47\) eV. Thus, irrespective of the crystal environment, Fe states are localised in CoFe\(_2\)O\(_4\). The Co states in the octahedral sites are, however, delocalised, particularly in the spin up band. The distortions associated with the Co site break the \( t_{2g} \) degeneracy only slightly. In the down spin band, the \( d_{zx},d_{zy} \) states give rise to states near the Fermi level (peaks close to \(-1\) eV). There were no such states associated with the octahedral sites in the other two compounds. The extra electrons in Co, in comparison to Cr and Mn, are responsible for these states. This, in turn, reduces the band gap, in comparison to CoCr\(_2\)O\(_4\); the calculated band gap of CoFe\(_2\)O\(_4\) being 1.14 eV. The \( t_{2g} \) states of Co are delocalised, hybridising with the oxygen \( p \) states. The magnetic moments are, therefore about 3 \( \mu_B \) and 4 \( \mu_B \) for Co and Fe\(_O\) in CoFe\(_2\)O\(_4\), (table 3).

The comparative study of the electronic structure, thus, shows that the Co states are delocalised irrespective of the crystal environment while the Fe states are extremely localised in the CoB\(_2\)O\(_4\) compounds considered. This would have important consequences on the magnetic exchange interactions and therefore the spin structures of the pristine compounds as well as in doped systems which have been investigated experimentally only recently [9, 12, 13]. In the next section we compute and discuss the magnetic exchange interactions of these compounds.

Table 3. The magnetic moments of A (\( \mu_A \)), B (\( \mu_B \)) cations and the total moment (\( \mu_T \)) per formula unit in Bohr magneton.

| System    | A site | \( \mu_A \) | B site | \( \mu_B \) | \( \mu_T \) |
|-----------|--------|-------------|--------|-------------|------------|
| CoCr\(_2\)O\(_4\) | Co     | -2.66       | Cr     | 2.94        | 2.95       |
| MnCr\(_2\)O\(_4\) | Co     | -2.68       | Mn     | 3.81        | 4.84       |
| CoFe\(_2\)O\(_4\) | Fe\(_T\) | -3.98       | Fe\(_O\) | 4.10        | 2.98       |
| Co\(_O\)     |        |             | Co\(_O\) | 2.66        |            |

Figure 7. The total (top panel) and site projected densities of states (A in the middle panel and B in the bottom panel along with anion contributions) for CoFe\(_2\)O\(_4\). The energies are plotted with respect to Fermi level.


### Table 4. The magnetic exchange parameters ($J_{ij}$ in meV) and the ferrimagnetic transition temperatures ($T_C$ in K) of the three compounds.

| System     | Type of AA pair | $J_{AA}$ | Type of BB pair | $J_{BB}$ | Type of AB pair | $J_{AB}$ | $T_C$  |
|------------|-----------------|----------|-----------------|----------|-----------------|----------|--------|
| CoCr$_2$O$_4$ | Co–Co           | −0.56    | Cr–Cr           | −3.01    | Co–Cr           | −3.26    | 144(97$^a$) |
| CoMn$_2$O$_4$ | Co–Co           | −0.29    | Mn–Mn           | −1.05(out of plane) | Co–Mn | −3.53 | 153(85$^a$) |
| CoFe$_2$O$_4$ | Fe$_{O}–$Fe$_{O}$ | −2.06    | Co$_{O}$–Co$_{O}$ | 0.08 | Fe$_{T}$–Co$_{O}$ | −10.43 | |
|             | Fe$_{O}$–Fe$_{O}$ |         | Fe$_{O}$–Fe$_{O}$ | −4.77 | Fe$_{T}$–Fe$_{O}$ | −21.65 | 1079(860$^a$) |
|             | Fe$_{O}$–Co$_{O}$ |         | Fe$_{O}$–Co$_{O}$ | 0.84 |

$^a$ Lawes et al [30]. $^b$ Wickham and Croft [31]. $^c$ Teillet et al [28].

#### 3.4. Magnetic exchange interactions

The magnetic exchange interactions are computed by mapping the GGA+U total energies of different collinear spin configurations on to a Heisenberg Hamiltonian [16]. The results for the nearest neighbour interactions are presented in table 4. The higher neighbour exchange interactions are smaller by an order of magnitude and hence they are not considered for discussions. The results show that the A–A interactions are the weakest and therefore, is not expected to play any significant role. This is consistent with the discussion by Kaplan [35]. In CoCr$_2$O$_4$, the A–B and B–B exchange interactions are comparable. In this case B site $t_{2g}$ orbitals are half-filled. So direct B–B interactions are possible, apart from the super-exchange via oxygen atoms. Moreover, nearly empty $e_g$ orbitals reduce the anion shielding as partial covalency via $e_g$ orbitals are possible. However, since the A site $t_{2g}$ orbitals are more than half-filled, partial covalency with anions is also not possible (as seen in the extremely localised Fe densities of states), leading to a large anion shielding and a subsequent reduction in the B–B interaction in comparison to the A–B interaction.

The ferrimagnetic transition temperatures ($T_C$) are calculated using these exchange interactions and under mean field approximation, as done in [16]. Our calculated results and a comparison with experimental values are presented in table 4. As expected, the critical temperatures calculated by a mean field approximation overestimates the values. However, the calculated values reproduce the trends seen in the experiments with CoFe$_2$O$_4$ having a large $T_C$ due to very large values of $J_{AB}$, while the other two have rather small values of $T_C$ due to competing $J_{AB}$ and $J_{BB}$ leading to non-collinear magnetic structures.

#### 4. Conclusions

We have performed systematic investigations into the structural and magnetic properties of CoB$_2$O$_4$ magnetic spinels by changing the B cation using first-principles density functional theory based methods. The understanding of the properties of these compounds is done by quantifying the relative strengths of the crystal field effect and the exchange effect through an analysis of their electronic structures. We find that the electron–electron interactions of the magnetic cations play a very important role and without the incorporation of this, the correct ground state structures cannot be obtained. The strong electron correlations are responsible for significant local structural distortions at the octahedral site and global tetragonal distortions for CoMn$_2$O$_4$. These are responsible for the trends in the electronic properties such as the band gap. The electronic structures of these compounds are significantly different as the B site cation is changed. This, in turn, affects the inter-atomic magnetic exchange interactions considerably and is responsible for very different spin structures of these.
systems. In this work, for the first time, understanding of the trends in the magnetic properties are attempted through proper quantification of the associated quantities and by providing necessary explanations from the trends in the local structural parameters and the electronic structures. The results hold immense significance with regard to the recent experimental results on Co(Cr\textsubscript{1−\(x\)}Fe\textsubscript{x})\textsubscript{2}O\textsubscript{4} and Co(Cr\textsubscript{1−\(x\)}Mn\textsubscript{x})\textsubscript{2}O\textsubscript{4} systems, where the chemical properties of the third magnetic atom in CoCr\textsubscript{2}O\textsubscript{4}, the sub-lattice occupancies and the structural distortions are thought to give rise to interesting functional properties. In future communications, these issues will be addressed.

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