First-principles investigations into the thermodynamics of cation disorder and its impact on electronic structure and magnetic properties of spinel Co(Cr$_{1-x}$Mn$_x$)$_2$O$_4$

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Abstract

Cation disorder over different crystallographic sites in spinel oxides is known to affect their properties. Recent experiments on Mn doped multiferroic CoCr$_2$O$_4$ indicate that a possible distribution of Mn atoms among tetrahedrally and octahedrally coordinated sites in the spinel lattice give rise to different variations in the structural parameters and saturation magnetisations in different concentration regimes of Mn atoms substituting the Cr. A composition dependent magnetic compensation behaviour points to the role conversions of the magnetic constituents. In this work, we have investigated the thermodynamics of cation disorder in Co(Cr$_{1-x}$Mn$_x$)$_2$O$_4$ system and its consequences on the structural, electronic and magnetic properties, using results from first-principles electronic structure calculations. We have computed the variations in the cation-disorder as a function of Mn concentration and the temperature and found that at the annealing temperature of the experiment many of the systems exhibit cation disorder. Our results support the interpretations of the experimental results regarding the qualitative variations in the sub-lattice occupancies and the associated magnetisation behaviour, with composition. We have analysed the variations in structural, magnetic and electronic properties of this system with variations in the compositions and the degree of cation disorder from the variations in their electronic structures and by using the ideas from crystal field theory. Our study provides a complete microscopic picture of the effects that are responsible for composition dependent behavioural differences of the properties of this system. This work lays down a general framework, based upon results from first-principles calculations, to understand and analyse the substitutional magnetic spinel oxides $A(B_{1-x}C_x)_2O_4$ in presence of cation disorder.

Keywords: oxides, spinel, cation disorder, electronic structure, magnetism, crystal field

(Some figures may appear in colour only in the online journal)
coordinated B. The degree of cation disorder is represented by a single parameter \( y \) which can take values between 0 and 1. The ‘normal spinel’ compounds are those with \( y = 0 \) when the \( A \) atoms in \( AB_2O_4 \) compounds occupy the tetrahedral sites and \( B \) atoms the octahedral sites. The ‘inverse spinel’ compounds are the ones with \( y = 1 \) where the tetrahedral sites are completely occupied by the \( B \) atoms, while the octahedral sites are occupied by equal amounts of \( A \) and \( B \) atoms. The degree of cation disorder in a material depends on experimental conditions such as the annealing temperature [11–13] or the control of the non-equilibrium disorder [15]. Various studies on a variety of spinels have established that the electrical [14, 15], electronic [16] and thermal [17, 18] properties of these compounds can be controlled by manipulating the degree of cation disorder. Thus, precise knowledge of the degree of cation disorder in a spinel compound is important to understand its fundamental properties.

Magnetic spinels with different magnetic constituent in \( A \) and \( B \) sub-lattices have gained prominence as they widen the scope of functionalities of spinel oxides arising out of different magnetic interactions. Moreover, magnetism offers greater perspectives regarding various degrees of freedom, such as the lattice and the magnetic ones [19, 20]. Recently discovered coupling between the charge and spin degrees of freedom, the multiferroic property, in a few chromite spinels [21–23], has generated considerable interests regarding the understanding of the structure-property relationships and subsequent discovery of new multiferroic materials with improved functionalities. Among these the oxide spinel \( \text{CoCrO}_2 \) is found to be a promising multiferroic material as it exhibits switchable electric polarisation under reversal of magnetic field [21]. The richness of its magnetic phase diagram comprising of various long range and short-range, collinear and non-collinear magnetic structures [24–27] prompted researchers to examine the effects of substitution of one of the magnetic atom with a new one on its properties. Subsequently, new and interesting phenomena like tunable exchange bias, temperature dependent magnetic compensation and magnetostriictions were observed upon control substitution of \( Cr \) with Fe atoms [28–31]. These novel phenomena were attributed to the composition dependent occupancy pattern of the substituted Fe atoms in \( \text{CoCrO}_2 \) which violated the empirical idea of expected occupancy pattern obtained from Mossbauer experiments [32] and also from the theoretical model based upon the relative sizes of cations [33].

The interesting structure-property relationship upon substitution of \( Cr \) atoms at \( B \) sites in \( \text{CoCr}_2O_4 \) with \( Mn \), led to a systematic investigation of \( Mn \) substituted \( \text{CoCr}_2O_4 \) [34]. The system \( \text{Co(Cr}_{1−x}\text{Mn}_x)_{2}O_4 \) is expected to provide interesting insights into the site preferences of the cations, and its associations with the changes in various properties as \( x \) increases. This is due to the fact that while \( \text{CoCr}_2O_4 \) has a cubic ground state (space group \( Fd\bar{3}m \)), \( \text{CoMn}_2O_4 \) is tetragonal with a significant elongation along \( z \) axis (space group \( I4/idxm \)) [11]; there is no evidence of any cation disorder in the former while non-negligible cation disorder (\( y = 0.22–0.39 \)) depending upon the annealing temperature is reported for the later [11, 35]. Investigations into the structural and magnetic properties [34] revealed a deviation in the variations of the lattice constant for smaller \( x \) values (\( x < 0.15 \)) from the expected linear increase with increasing \( x \), a structural distortion for \( x > 0.7 \), a magnetic compensation at \( x \sim 0.25 \), and three different patterns of variations in magnetisations depending upon the ranges of \( x \). The authors addressed this non-regular behaviour in the lattice constants and the magnetisation along with the phenomena of composition dependent magnetic compensation to the varying trends in the site preferences of the Mn atoms substituting the \( Cr \). They explained the trends in the properties by assuming that the substituting \( Mn \) atoms first occupy the tetrahedral \( A \) sites up to the compensation point, and then they first occupy one of the \( B \) sites till a critical value of \( x \) and finally occupy the other \( B \) site upon further increase in \( x \). However, this investigation neither quantified the cation disorder, nor provided any microscopic picture behind the non-regular behaviours.

With a motivation to understand the observed non-regular phenomena in \( \text{Co(Cr}_{1−x}\text{Mn}_x)_{2}O_4 \) from microscopic point of view and thus interpret them with a robust framework, in this work, we provide a detailed account of the composition dependences and thermodynamics of the cation disorder in \( \text{Co(Cr}_{1−x}\text{Mn}_x)_{2}O_4 \) by combining density functional theory (DFT) based first-principles calculations and a thermodynamic model. These first-principles calculation based results substantiate the experimental claim of the site preferences of the \( Mn \) atoms by putting it on a solid theoretical ground. Concurrently, a systematic study of the structural, magnetic and electronic properties as a function of composition and degree of cation disorder is carried out. These results are interpreted in terms of the elements in the crystal field theory and the electronic structures, thus presenting the necessary microscopic picture governing the physics of this system. In section 2, we present details of the models and the computational techniques. The results are presented in section 3, followed by the conclusions.

2. Details of calculations

In an \( AB_2O_4 \) spinel, like \( \text{CoCr}_2O_4 \), with no cation disorder between the sub-lattices, the tetrahedral sites are occupied by the \( A \) atoms in +2 charge state and the octahedral sites are occupied by the \( B \) atoms in +3 charge state. In case of cation disorder between the sub-lattices where degree of cation disorder is denoted by the parameter \( y \), the tetrahedral sites consist of a binary alloy \( A_{1−y}B_y \) and each of the octahedral sites has the composition \( A_{1/2}B_{1−y/2} \). The degree of cation disorder \( y \) at a finite temperature \( T \) can be calculated from the thermodynamic consideration of cation distributions by treating it as a simple chemical equilibrium [36]. Such modelling has been proved to agree reasonably well with the experiments in most of the cases [15, 37–42]. In this model, the configurational free energy of cation disorder per formula unit \( \Delta F \) is given as

\[
\Delta F = E_c - T \Delta S_c
\]

\( E_c \) is the cation disorder energy per formula unit. \( T \) the temperature and \( \Delta S_c \) the configurational entropy which is calculated using the general formula \( \Delta S_c = -k_B \sum_{i,b} p_i^b \ln p_i^b \); \( p_i^b \) is the
concentration of the cation $b$ at the $i$th sub-lattice. The equilibrium degree of cation disorder parameter $y_0$ at the given temperature $T$ can, then, be obtained by minimising $\Delta F$ with respect to $y$. We have generalized this thermodynamic model in the present context and used it in conjunction with first-principles electronic structure methods to obtain the composition dependences of $y_0$ along with the structural, electronic and magnetic properties as a function of composition and degree of cation disorder. Details of the modelling and calculations are given in section I of supplementary material (stacks.iop.org/JPhysCM/29/055805/mmedia).

3. Results and discussions

3.1. Temperature and concentration dependences of degree of cation disorder $y$

Before discussion of the physical properties of $\text{Co(Cr}_{1-y}\text{Mn}_y\text{)}\text{O}_4$, it is required to find out the degrees of cation disorder between Co and Mn as a function of Mn concentration $x$ and the temperature $T$. The temperature dependence is important because earlier works on various spinel compounds have demonstrated that $y$ may be quite sensitive to the annealing temperature [12, 13, 41, 42]. In figure 1 we show the dependences of the cation disorder energy $E_c$ and the configurational free energy of cation disorder $\Delta F$ on $y$ for different Mn concentration $x$, at a temperature $1500\,\text{K}$ which is close to the annealing temperature of $1523\,\text{K}$ reported in the experiment [34]. The nature of variations in $E_c$ with $y$ is almost identical for all $x$ except $x = 0.25$. In all cases except $x = 0.25$, $E_c$ increases with $y$. In case of $x = 0.25$, $E_c(y = 1) < E_c(y = 0.5)$, the difference being only about $3\,\text{meV per formula unit}$. The reason for this can be analysed from the electronic structures and is discussed in section 3.4. We find that the cation disorder is zero for all values of $x$ if we do not consider the configurational entropy. This implies that all substituting Mn atoms will be occupying the octahedral sites if the effect of the entropy is not included. Upon inclusion of the entropy term, states with cation disorder that is with non-zero values of parameter $y$ are stabilised. We find that the larger contribution of the entropy as $x$ increases, particularly for $y = 0.5$ where disorder at the sub-lattices are maximum, overcompensates the sharp increase in $E_c$ with $y$, thus stabilising states with non-zero values of $y$. The results suggest that the equilibrium value of $y$ at which $\Delta F$ is a minimum goes towards 0 as $x$ increases till 0.5, that is, up to the composition when the Cr and Mn contents in the system are identical. Further increase in the Mn content that is at $x = 0.75$ increases the equilibrium value of $y$ before it is further reduced when the Mn substitution is complete at $x = 1$. The quantitative variations of $y_0$, the equilibrium value of $y$, with temperature $T$, presented in figure 2, shows this qualitative behaviour clearly. At $1500\,\text{K}$, $y_0 = 0.4$, 0.26, 0.17 and nearly 0 for $x = 0.0625$, 0.125, 0.25 and 0.5 respectively. At $x = 0.75$, the value of $y_0$ is 0.28 which decreases to 0.13 when $x = 1$. This result, thus, suggests that in the beginning of Mn substitution in $\text{CoCr}_2\text{O}_4$, a significant amount of Mn prefers to occupy the tetrahedral positions, instead of the expected octahedral ones. As the Mn content increases, more and more Mn occupies the octahedral positions until one reaches the point where the Mn content is equal to Cr content ($x = 0.5$). Further increase in Mn content initially puts some of it again in the tetrahedral sites, only to provide more preferences to the octahedral sites as the content increases towards complete substitution of Cr. The importance of this result is that it supports the qualitative picture of site
occupancies as conjectured in the experiments [34]. The differences with the picture provided by the experimentalists is that they did not predict the re-emergence of the phenomenon of Mn atoms preference to tetrahedral sites after a critical composition. In the next sections we will provide an explanation of this. The other important outcome of the thermodynamics of cation disorder is that the degree of cation disorder in this system is not very robust as can be made out from the substantial variations in \( y_0 \) with temperature. For any value of \( x, y_0 \) decreases continuously towards 0, and at room temperature the cation disorder for most of the compositions are insignificant. As cation disorder is suggested to be the reason behind non-regular behaviours of magnetisation and phenomenon such as magnetic compensation [34], the importance of our results is that it provides the temperature range over which the degree of cation disorder is appreciable and hence the experimental preparation of the samples should be done accordingly. This also suggests that the cation disorder in these systems can be manipulated by controlling the temperatures. Such manipulations of cation disorder can substantially affect functional properties like the electrical conductivity as has been seen elsewhere [15].

3.2. Structural parameters and their variations with \( x \) and \( y \)

The first signature of cation disorder upon Mn substitution in CoCr\(_2\)O\(_4\) was noted from the non-regular variations in their measured lattice constants with increasing Mn content, in the low Mn content regime [34]. If the Mn, expected to be in +3 charge state, had occupied the octahedral sites from the beginning, the lattice constant should have increased linearly with Mn content \( x \) as Mn atoms have larger ionic radii than Cr at octahedral sites [33]. We, therefore, first discuss the variations in the structural parameters with concentration of Mn as well as with variations in the degree of cation disorder. In table 1, we present various cation–anion bond distances at sites of different symmetries and their variations with \( x \) and \( y \). The lattice constants and the cation–anion bond distances are obtained from the DFT+U calculations. The oxygen parameters are then obtained as [43]

\[
u = -11 + 6r^2 + \frac{\sqrt{33}r^2 - 8}{24(r^2 - 1)}
\]

where \( r = \frac{R_{\text{oct}}}{R_{\text{tet}}} \), the ratio of the average cation–anion bond distances at the octahedral and the tetrahedral sites; \( R_{\text{oct}}, R_{\text{tet}} \) are obtained by concentration averages of individual cation–anion bond distances. The lattice constants \( a \) and \( c \) along with the oxygen parameters \( u, a, \) for various \( x \) and \( y \) are presented in table III, supplementary material. The results show that for \( x \) up to 0.5, the systems retain the cubic structure for all degrees of cation disorder, in agreement with the experiments. For \( x = 0.75 \) and 1, a structural distortion leading to tetragonal phases are obtained, again in agreement with the experimental observations. Quantitatively, the lattice constants calculated by DFT+U are about 1-1.5% higher than the experimentally measured ones. This is due to the choice of generalised gradient approximation (GGA) [44] in describing the exchange-correlation part of the Hamiltonian. However, the qualitative agreement with the experiments is reasonably good, with a small increase in lattice constants with \( x \) up to 0.5. It is to be noted that the experimentally observed deviation in the lattice constant \( a \) from the expected linear behaviour was for very small range of \( x \) \( (0 < x < 0.25) \) and the maximum change was only about 0.1%. The maximum change in the DFT+U calculated lattice constant for the range \( x = 0–0.25 \)

![Table 1: Calculated cation–anion bond distances (in Å) in Co(Cr\(_{1–x}\)Mn\(_x\))\(_2\)O\(_4\) for different \( x \) and \( y \) values.](image)

| \( x \) | \( y \) | \( x \) | \( y \) | \( x \) | \( y \) | \( x \) | \( y \) |
|---|---|---|---|---|---|---|---|
| 0  | 0  | 2.00 | —  | 2.01 | —  | 2.01 | —  |
| 0.0625 | 0.5 | 2.00 | 2.04 | 2.01 | 1.98 | 2.10 | —  |
| 1  | 0  | 2.00 | 2.04 | 2.01 | —  | 2.10 | —  |
| 0  | 0  | 2.00 | —  | 2.01 | 2.06 | —  | —  |
| 0.125 | 0.5 | 2.00 | 2.04 | 2.01 | 1.97 | 1.97 | —  |
| 1  | 0  | 1.99 | 2.03 | 2.01 | —  | 1.97 | —  |
| 0  | 0  | 2.00 | —  | 2.01 | 2.07 | —  | —  |
| 0.25 | 0.5 | 2.00 | 2.04 | 2.01 | 2.07 | 1.97 | —  |
| 1  | 0  | 1.99 | 2.03 | 2.01 | —  | 1.96 | —  |
| 0  | 0  | 2.00 | 2.04 | 2.01 | 2.07 | 1.95 | —  |
| 0.5 | 0.5 | 2.00 | 2.04 | 2.01 | 2.07 | 1.95 | —  |
| 1  | 0  | 1.99 | 2.03 | 2.01 | —  | 1.95 | —  |
| 0  | 0  | 1.99 | —  | 2.01 | 2.1 \pm 0.15 | —  | —  |
| 0.75 | 0.5 | 2.00 | 2.04 | 2.01 | 2.06 \pm 0.1 | 2.09 \pm 0.03 | —  |
| 1  | 0  | 2.02 | 2.03 | 2.02 | 2.10 | 2.03 \pm 0.04 | —  |
| 0  | 0  | 1.99 | —  | 2.13 \pm 0.17 | —  | —  | —  |
| 0.5 | 0.5 | 2.00 | 2.04 \pm 0.04 | 2.13 \pm 0.13 | 2.13 \pm 0.07 | —  | —  |
| 1  | 0  | 2.02 | 2.03 | 2.12 \pm 0.14 | 2.04 \pm 0.12 | —  | —  |
is about 0.3\%, if we compare results of $y = 0$ only. The compar-
is of results with cation disorder $y = 0$ only is justified as we see that between $x = 0$–0.125, the lattice constant $a$ does not change between $y = 0$ and $y = 0.5$ and that the equilibrium degree of inversion $y_0$ is well within this range of $y$ moving towards $y = 0$ as $x$ increases. For the concentrations $x = 0.75$, 1, we find that the qualitative nature of variations in the lattice parameters ($c$ increases while $a$ decreases) with $x$ is in agreement with the experiment. For $x = 1$, the $c/a$ ratio (for $y = 0$) obtained in our calculations is 1.12 which agrees very well with the experimental value of 1.09 [34]. We also find that the $c/a$ ratio decreases to 1.1 when $y = 0.5$. Since our calculated equilibrium $y$ is in between 0 and 0.5, the agreement with experiment would have been better had we considered the actual $y_0$ for the calculations. For $x = 0.75$, the calculated $c/a$ ratio varies from 1.1 to 1.04 as $y$ varies from 0 to 0.5 while the experimental value is 1.07. Thus our results qualitatively agree with the experiments as the calculated $y_0$ at this concentration is in between $y = 0$ and $y = 0.5$. Comparison of our calculated $u$ parameters with experimental results for an arbitrary $x$ is not possible due to unavailability of reported experimental values. The comparisons can be made only for the end compounds. For CoCr$_2$O$_4$, the calculated $u$ value of 0.262 agrees well with the experimental value of 0.264 [25]. For CoMn$_2$O$_4$, the calculated values of 0.255 and 0.267 for $u_t$ and $u_g$ ($y = 0$), respectively, agree reasonably well with the experimental results of 0.230 and 0.261 [11]. Thus, overall, our calculated structural parameters and their trends with $x$ are consistent with the trends of calculated $y_0$ with variations in $x$. The variations of the lattice parameters with degree of cation disorder too, can be understood from the variations in various bond distances with $x$ and $y$. It has been elaborated in supplementary material, section II.

We now try to provide explanations as to why the Co-O octahedral bond distances reduce dramatically for certain concentrations and degrees of cation disorder. It is expected that Co at both sites will be having a +2 charge state. In that case, the effective ionic radius of Co should be 0.75 Å at octahedral site and 0.58 Å at tetrahedral sites [33]. The Co-O bond distances at tetrahedral sites, thus, would be considerably lower than that for Co at octahedral sites. Our calculations are consistent with this for $x = 0.0625$ for all degrees of cation disorder. For $x = 0.125, 0.25$ and 0.5, and for $y = 0$, our calculations show the opposite trend. This indicates that the Co at octahedral sites for these cases would either be in a +2 charge state with low spin or in a +3 charge state with either high or low spin (The effective ionic radii of Co$^{2+}$ in low spin state, Co$^{3+}$ in high spin state and Co$^{3+}$ in low spin states are 0.65 Å, 0.61 Å and 0.55 Å [33] respectively.). From elementary crystal field theory [45], it is known that the OSPE of a $d^7$ configuration is more than that of a $d^8$ configuration in high spin state, while it is exactly opposite for a low spin state. Thus, the octahedral Co atoms for these $x$ and $y$ parameters are expected to be in a low spin +3 state ($d^8$ configuration). The results on magnetic moments, and the electronic structures, discussed in next sections confirm this and will be dealt in more detail.

The reason behind the tetragonal deformations at $x = 0.75$, 1 can also be understood from the crystal field theory. In a comprehensive work, Dunitz and Orgel [46] had attributed the electronic configurations at the octahedral and tetrahedral sites to the degrees of distortion from cubic symmetry in spinels. Counting the average number of $t_{2g}$ and $e_g$ electrons of tetra-
hedral and octahedral sites obtained from the charge states of the cations, we find that for $y = 0$, the octahedral sites have $(t_{2g})^6(e_g)$ like configurations, which will give rise to a large distortion in order to lift the degeneracy associated with the $e_g$ states. With increase in the cation disorder, the presence of Co atoms in the octahedral site reduces the degeneracies associated with the $e_g$ orbitals. Thus, the degree of tetragonal distortions decrease as is seen from our calculated results of decreasing $c/a$ with increasing $y$.

Finally, we try to explain the reason behind re-appearance of non-negligible cation disorder at $x = 0.75$ after it had reduced to zero at $x = 0.5$. The arguments are based upon the bond distance results and elements of crystal field theory. From table I, we find that up to $x = 0.5$, octahedral Mn-O bond distances were constant for $y = 0$ state. At $x = 0.75$, these bond lengths increase as a whole. From elementary crystal field theory, we know that the crystal field parameter $\Delta$ at octahedral site is inversely proportional to the cation–anion distance $R$ ($\Delta \sim R^{-5}$) [45]. Thus, when the Mn-O bonds increase in lengths at $x = 0.75$, the corresponding octahedral crystal field will become weaker in comparison to that for other concentrations significantly. Consequently, the octa-
hedral crystal field stabilisation energy for the Mn atoms will reduce as it is decided by the strength of $\Delta$, resulting in an increased preference of Mn atoms towards tetrahedral sites at $x = 0.75$ in comparison to $x = 0.5$. This is exactly reflected in the re-emergence of non-zero $y_0$ at $x = 0.75$. In the next sections we provide more conclusive evidences of the possible charge and spin states of various atoms in different crystal sites which will corroborate the explanations given here.

3.3. Magnetic properties and their dependencies on $x$ and $y$

The magnetisation measurements [34] on Co(4Cr$_{1-y}$Mn$_y$)$_{12}$O$_{12}$ show three distinct compositions ranges where the variations of magnetisations with composition are different, although in all three regions, the variations are linear. For $x = 0$–0.25, the magnetisation decreases and reaches the point of magnetic compensation. Further increase of $x$ shows a linearly increasing magnetisation till another critical point $x \sim 0.65$ after which the magnetisation decreases again with increase in Mn content. The explanation of this behaviour was based upon the canted spin structures observed in CoCr$_2$O$_4$ [24] and CoMn$_2$O$_4$ [11]. The authors of [34] considered that like CoCr$_2$O$_4$, the canted spin structure will have opposing spin alignments at the two octahedral sites with one of them (site $B_1$) aligning with the tetrahedral site. The magnetic compensa-
tion behaviour was, thus, attributed to the initial occupation of Mn atoms at both tetrahedral and the other octahedral site $B_2$ with opposing spin alignments, thus, cancelling the net moment as Mn content is increased. The reason behind
and Mn would have a greater preference towards Co per formula unit) of CrMnO which is consistent effects of Mn atoms at 2 sites gradually, till the next critical B point, after which the extra Mn atoms start occupying the entire range of material) suggest non-collinear spin structures throughout the changes in x. As expected, the moment of tetrahedral Co of tetrahedral Mn and tetrahedral Co are insensitive to the y

Table 2 presents the results on atomic and total magnetic

ture in order to interpret the experimental results qualitatively. The results obtained from calculations on collinear Neel struc-
tion [34].

Before interpreting the experimental results and checking the validity of the arguments given in [34] a look at the nearest neighbour inter-atomic magnetic exchange interactions \( J_{ij} \) for different x is necessary. The results (section III, supplementary material) suggest non-collinear spin structures throughout the entire range of x as in agreement with experimental suggestion [34].

Since it is extremely difficult to model these non-collinear spin structures, particularly since no experimental information is available for Mn substituted samples, we took recourse to the results obtained from calculations on collinear Neel structure in order to interpret the experimental results qualitatively. Table 2 presents the results on atomic and total magnetic moments (in \( \mu_B \) per formula unit) of Co(Cr\(_{1-x}\)Mn\(_x\))O\(_2\) for different concentrations x of Mn and for various degrees of cation disorder y.

| x  | y  | \( \mu_{Co} \) | \( \mu_{Mn} \) | \( \mu_{Cr} \) | \( \mu_{Mn} \) | \( \mu_{Co} \) | \( \mu_T \) |
|----|----|----------------|----------------|----------------|----------------|----------------|--------------|
| 0  | 0  | -2.68          | -              | 2.95           | -              | -              | 2.95         |
| 0.0625 | 0   | -2.68          | -4.50          | 2.95           | 3.23           | 2.71           | 2.84         |
| 1  | 0  | -2.68          | -              | 2.95           | 3.87           | -              | 3.07         |
| 0.125 | 0   | -2.68          | -4.50          | 2.95           | 3.41           | 2.71           | 2.73         |
| 0  | 0  | -2.68          | -              | 2.95           | 3.86           | -              | 3.41         |
| 0.25 | 0   | -2.68          | -4.50          | 2.93           | 3.84           | 0.05           | 2.00         |
| 1  | 0  | -2.68          | -              | 2.91           | -              | 0.02           | 0.58         |
| 0  | 0  | -2.67          | -4.49          | 2.94           | 3.83           | -              | 3.89         |
| 1  | 0  | -2.68          | -              | 2.93           | 3.81           | 0.00           | 1.05         |
| 0.75 | 0   | -2.68          | -4.48          | 2.89           | 3.80           | 2.72           | 2.53         |
| 1  | 0  | -2.69          | -              | 2.88           | 3.80           | 3.07           | 3.04         |
| 1  | 0  | -2.71          | -4.48          | 2.89           | 3.80           | -              | 4.84         |
| 1  | 0  | -2.68          | -              | 3.70           | 3.70           | 2.71           | 3.01         |
| 1  | 0  | -4.39          | -              | 3.78           | 3.70           | 3.07           | 3.02         |

increase of the magnetisation after compensation was thought of due to Mn atoms occupying \( B_1 \) sites, diminishing the effects of Mn atoms at \( B_2 \) sites gradually, till the next critical point, after which the extra Mn atoms start occupying the \( B_2 \) sites again, bringing a decreasing trend in magnetisation as x increases. The experimentalists, however, did not substantiate their claim with detailed calculations. Their magnetisation measurements also indicated that the canting angles changed upon Mn substitution.

Before interpreting the experimental results and checking the validity of the arguments given in [34] a look at the nearest neighbour inter-atomic magnetic exchange interactions \( J_{ij} \) for different x is necessary. The results (section III, supplementary material) suggest non-collinear spin structures throughout the entire range of x as in agreement with experimental suggestion [34].

The much greater OSPE of high spin Mn\(^{3+} \) and Cr\(^{3+} \) states in comparison to Mn\(^{2+} \) are responsible for this. The Co atoms at the octahedral positions oscillate between high spin and low spin states depending upon x and y. For x = 0.0625, irrespective of the degree of cation disorder, the octahedral Co are in high spin and +2 charge states as is reflected in their moments being \( \sim 3 \mu_B \). For x = 0.125, while 50% of cation disorder (y = 0.5) still keeps Co spin and charge states same, complete ‘inversion’ (y = 1) quenches the Co moment leading to a low spin state with moment \( \sim 0 \). This trend continues till x = 0.5 and is independent of the degree of cation disorder. The high spin state is regained at x = 0.75 and remains intact for x = 1 with \( \mu_{Co} \sim 3 \mu_B \) irrespective of the degree of cation disorder. As was argued in the previous section, the relative OSPE values [45] for Co\(^{2+} \) and Co\(^{3+} \) clearly demonstrate that in the low spin state, Co\(^{3+} \) would have a greater preference towards octahedral sites. One can relate the octahedral Co-O bond distances (table 1) with the low spin +3 charge state in this case using elementary crystal field theory. The significant decrease in octahedral Co-O bond distances for a range of x and y, increases the octahedral Co crystal field. As a result these Co pair up the electrons. As the magnetic moment is close to zero, the configuration must be \((e_g)^6 (e_g)^3 \) which is consistent with the preferred +3 charge state as predicted from results on OSPE. The regaining of the high spin state at x = 0.75 can be
understood from the increase in Co-O octahedral bond lengths due to the structural relaxations, and subsequent weakening of the octahedral Co crystal field. As was mentioned earlier, due to the low spin state of octahedral Co while the rest of the atoms at different sites are in high spin states, an additional magnetic entropy of $2k_B \ln 2$ is added to $\Delta F$ for the select $x$ and $y$ values. A non-zero $y_0$ value for these concentrations are obtained only if this magnetic entropy term is added. Thus, a cation disordered state at these concentrations is driven by the changes in the magnetic entropy.

Although the results are for collinear spin arrangements, in conjunction with the calculated $y_0$ values for each $x$, a qualitative variation in the total magnetic moment quite similar to the experimentally observed can be extracted by careful analysis of the results. Since $y_0$ for $x = 0.0625$ is $\sim 0.4$, the expected magnetic moment would be close to $2.84 \mu_B$, the calculated value for $y = 0.5$. As the $y$ is in the range of 0.17–0.4 for $x$ up to 0.25, the expected values of magnetic moments may show a decreasing trend as $x$ increases. An increase in the moment upon further increase of $x$, that is in the range $0.25 < x < 0.75$, is expected as the $y_0$ continuously reduces making the cation disorder close to zero, and thus the appropriate moments to look at from table 2 would be the ones with $y = 0$ which shows continuous increase with $x$. Our results in the range $x = 0.75–1$, however, do not quite seem to follow experimental behaviour qualitatively. At $x = 0.75$, the magnetic moment when $y = 0.28$, the $y_0$ value at this concentration, should be close to $3.5 \mu_B$ if the results between $y = 1$ and $y = 0.5$ are interpolated. This will indicate a decrease of moment as $x$ changes from 0.5 to 0.75 agreeing with the experimental behaviour. But the same interpolation in case of $x = 1$ puts the magnetic moment at this concentration close to $4.5 \mu_B$ which means an increase with respect to result at $x = 0.75$, in contradiction to the experimental trend. In spite of this disagreement, it is interesting that the results from collinear spin arrangement follow the experimental trend for a significant range of composition.

A qualitative model explaining the trends in the experimentally measured magnetisation can now be constructed by using the calculated atomic moments, the site occupancy patterns (table I, supplementary material) and the alignments of sub-lattice spins obtained in the experiments. The experimental spin structure makes a distinction between two octahedral sub-lattices which our collinear spin arrangement does not. If instead of considering the occupancies of both octahedral sub-lattices to be identical, we consider that after part of the octahedral sub-lattice spins obtained in the experiments. Since the moment upon further increase of $x$, that is in the range $0.25 < x < 0.75$, is expected as the $y_0$ continuously reduces making the cation disorder close to zero, and thus the appropriate moments to look at from table 2 would be the ones with $y = 0$ which shows continuous increase with $x$. Our results in the range $x = 0.75–1$, however, do not quite seem to follow experimental behaviour qualitatively. At $x = 0.75$, the magnetic moment when $y = 0.28$, the $y_0$ value at this concentration, should be close to $3.5 \mu_B$ if the results between $y = 1$ and $y = 0.5$ are interpolated. This will indicate a decrease of moment as $x$ changes from 0.5 to 0.75 agreeing with the experimental behaviour. But the same interpolation in case of $x = 1$ puts the magnetic moment at this concentration close to $4.5 \mu_B$ which means an increase with respect to result at $x = 0.75$, in contradiction to the experimental trend. In spite of this disagreement, it is interesting that the results from collinear spin arrangement follow the experimental trend for a significant range of composition.

A qualitative model explaining the trends in the experimentally measured magnetisation can now be constructed by using the calculated atomic moments, the site occupancy patterns (table I, supplementary material) and the alignments of sub-lattice spins obtained in the experiments. The experimental spin structure makes a distinction between two octahedral sub-lattices which our collinear spin arrangement does not. If instead of considering the occupancies of both octahedral sub-lattices to be identical, we consider that after part of Mn occupying the tetrahedral sites in accordance with the pattern depicted (table I, supplementary material), the rest of the Mn for a given $x$ completely occupies the $B_2$ sub-lattice which is anti-aligning with the other octahedral $B_1$ and the tetrahedral sub-lattice, then the experimental trends of magnetisation for $x = 0–0.25$ is qualitatively reproduced. This can be understood the following way: if we consider the DFT calculated atomic magnetic moments as the moments of individual atoms in this picture and consider that the $B_2$ sub-lattice has Cr and Mn while $B_1$ has Co and Cr, and the $y$ value for each $x$ is taken...
to be equal to that of the calculated $y_0$, then with increase in $x$, the contribution of $B_2$ sub-lattice will gradually increase in comparison to the other two which will reduce the net magnetic moment steadily. The increasing dominance of $B_2$ will be due to the fact that with increase in $x$, the $y$ steadily decreases and with rather small $x$, the content of Mn at the tetrahedral site is always small. Since octahedral Cr and tetrahedral Co have identical moments, their moments from $B_2$ and the tetrahedral sites will nearly cancel each other. Mn being the carrier of larger magnetic moments would have the maximum effect. Thus the Mn at $B_2$ site would control the magnetisation variation in this concentration range. With further increase in $x$, the $y$ value is supposed to be getting smaller and nearly vanish for $x = 0.5$. Thus, in the concentration range $x = 0.25$–0.5, the Mn is going to occupy the octahedral sites mostly. If we now once again let the occupancies of the two octahedral sites be different with most of the extra Mn occupying the $B_1$ site, then the magnetic moment of the system will increase as $x$ increases. This is because of the fact that since the occupancy of $B_1$ sub-lattice would not change much from what it was for $x = 0–0.25$, more Mn content at $B_1$ site with their spins anti-aligning to those of Mn in $B_2$ site would increase the total moment as the spins of $B_1$ and the tetrahedral sites align. This occupancy pattern would continue till $x = 0.5$ and possibly a little further up till about the critical point ($x \approx 0.7$) observed experimentally. Since $y = 0$ when $x = 0.5$, the expected occupancies in tetrahedral sub-lattice will be Co only, while both octahedral sub-lattices will have equal amounts of Cr and Mn. With further increase in $x$ and with expected $y$ value nearly zero, $B_2$ will have equal amounts of Cr and Mn and $B_1$ will be Mn rich Mn-Cr alloy, thus shooting up the magnetic moment further. At $x = 0.75$, the cation disorder returns. Now the cation disorder will be between tetrahedral and $B_1$ sites, with Co occupying the $B_1$ sites but the extra Mn mostly occupies the $B_2$ sites. As a result, the total moment steadily decreases as $x$ increases. This picture, thus, not only supports what was espoused by the experimentalists, but also puts it on a solid theoretical footing by using information from first-principles calculations.

### 3.4. Electronic structures and their variations with $x$ and $y$

Finally we present results on the electronic structures with variations in $x$ for three degrees of cation disorder represented by $y = 0, 0.5$ and 1 in figures 3–5 respectively. For the ‘normal spinel’ configuration ($y = 0$), the significant changes with Mn content happen in the majority (spin up) band, where Mn states occupy the states near Fermi level moving the Cr states to lower energies. At low concentrations of Mn, sharp peaks corresponding to half-filled $e_g$ states, are observed on both sides of Fermi level which smear with increase in the Mn content. The Mn and Co states dominate the majority band with increasing $x$ as expected. The Mn $t_{2g}$ contributions are around 3–4 eV below Fermi level, the Co $e_g$ states contribute mostly around 2–3 eV below Fermi level. The minority band consists of Co for energies below Fermi level. Thus, across the concentration range, Co is in a $+2$ state with fully filled $e_g$ and half-filled $t_{2g}$ orbitals, Cr is in a $+3$ state with half-filled $t_{2g}$ and empty $e_g$ orbitals and Mn is in a $+3$ state with completely filled $t_{2g}$ and half-filled $e_g$ orbitals. Each of the three atoms retain their characteristics across the concentration range with the peaks corresponding to each of them occurring in distinctly separate energy regions. Due to the appearance of Mn states in the gap after Fermi level, the band gap decreases with $x$ up to 0.5 (table V, supplementary material). For $x = 0.75$ and 1, the band gap again increases due to changes in the characteristics of the densities of states with the structural distortions. This is due to the shift of the Mn states near Fermi level and in the occupied part towards lower energy. At these concentrations, the majority and minority bands localise more, opening a larger gap. However, in going from CoCr$_2$O$_4$ to CoMn$_2$O$_4$, the band gap reduces considerably, due to the more delocalised Mn states as is apparent from the electronic structures presented here.

With 50% cation disorder ($y = 0.5$), new and interesting features appear in the electronic structures. Like $y = 0$, we have sharp $e_g$ peaks coming from octahedral Mn atoms in the unoccupied part of the majority band close to the Fermi energy for $x = 0.0625$ and 0.125. The contributions close to Fermi energy in the occupied part of the majority band now comes from $e_g$ states of Co at the octahedral sites. The octahedral Mn contribution in the unoccupied part moves towards the Fermi level as $x$ changes from 0.0625 to 0.125, thus reducing the band gap, as happened for $y = 0$ case. For these concentrations, the minority states near the Fermi level are made up of $t_{2g}$ orbitals of octahedral Co and $t_{2g}$ states of tetrahedral Mn atoms. At these concentrations, both octahedral and tetrahedral Co atom densities of states show completely filled $e_g$ and half-filled $t_{2g}$ orbitals. Thus Co at both sub-lattices are in $+2$ charge state. The densities of states significantly change at $x = 0.25$ and continue to be so at $x = 0.5$. Now, the majority states in the occupied and unoccupied parts closest to the Fermi level are again due to the octahedral Mn atoms which increases the band gap in comparison to that at $x = 0.125$. This happens as octahedral Co states in the majority band are sharply localised accommodating only the $t_{2g}$ electrons. The $t_{2g}$ states are now in the unoccupied part of the majority band and lie around 1–1.5 eV above Fermi level. The minority octahedral Co states consist of $t_{2g}$ in the occupied part and $e_g$ in the unoccupied part. Thus, the $t_{2g}$ orbitals of octahedral Co are completely full and the $e_g$ orbitals are completely empty. The octahedral Co atoms, therefore, are in low spin states and in a $+3$ charge configuration. This is consistent with our results on magnetic moments and the explanations based upon bond lengths. The strong splitting and localisations of the $e_g$ and $t_{2g}$ states also signify a stronger crystal field. The features in the electronic structures, thus, support our arguments based upon crystal field theory given in earlier sections. As a consequence, the band gaps increase from its value at $x = 0.125$. The densities of states again change substantially with $x = 0.75$ onwards. The localised octahedral Co $t_{2g}$ states for $x = 0.25, 0.5$ now delocalise considerably. The contributions due to $e_g$ states of octahedral Co appear at lower energies (at about $-6$ eV) indicating reduction of the crystal field and return of octahedral
Co to a +2 charge state. For these concentrations octahedral Mn start occupying the majority states near Fermi level and with a larger structural distortion at $x = 1$ in comparison to $x = 0.75$, the octahedral Mn $e_g$ states get energetically closer, reducing the band gap. Thus the band gap reduces to zero at $x = 1$. The highlights in the densities of states of the other component in the cation disorder, the Mn atoms at the tetrahedral site, have completely filled $t_{2g}$ and $e_g$ states in the minority spin channel along with completely empty major spin channel. This implies that the electronic configuration of this Mn would be $(e_g^3t_{2g}^3)$, a +2 charge state. Once again the results of the electronic structure confirm our picture on charge states as was discussed in earlier sections.

With ‘complete inversion’ that is for $y = 1$, we now see larger splittings in the majority bands for any given concentration, in comparison to $y = 0$, 0.5. Now the octahedral sites consist of only Cr and Co atoms upto $x = 0.5$. In [48], the octahedral crystal field parameters of Cr and Mn were calculated from first-principles. These were extracted from the pristine CoCrO$_2$ and CoMnO$_2$. The results showed that the crystal field of Cr is much stronger than that of Mn. In here, we have seen that the states on either side of the Fermi level are occupied by the octahedral atoms. Thus, when the octahedral sites are occupied by primarily Cr, its strong crystal field makes the band gaps larger in comparison to those for other degrees of cation disorder. With increasing Cr substitution, the crystal field at the octahedral site starts losing its strength, a signature of which is in the appearances of octahedral Co $e_g$ states between 1–2 eV above Fermi level. Consequently, the band gap decreases with increase in Mn concentration. A significant reduction in the band gap is observed when $x$ changes from 0.5 to 0.75. In this case, the Mn atoms have started to occupy the octahedral sites which reduces the crystal field further. However, another interesting feature of the densities of states at this concentration is that the tetrahedral Co states in the majority bands are now localised at a significantly lower energy region. Concurrently, there are more states of tetrahedral Co in the unoccupied part of the minority band at energies closer to the Fermi level. This is the reason behind drastic reduction in the band gap. This happens due to the alteration in the charge state of octahedral Co. Upto $x = 0.5$, this Co was in a low spin state due to the strong crystal field which paired all $t_{2g}$ electrons leaving $e_g$ states empty. A inspection of the densities of states reveal that the crystal field is still strong with a significant splitting of $e_g$ and $t_{2g}$ states. Moreover, a comparison of octahedral Co densities of states for $y = 0.5$ and $y = 1$ for this concentration show that in case of $y = 0.5$, the minority band had more densities of states in the energy region $0.5$ to $2$ eV below Fermi level. This implies that for $y = 1$, the octahedral Co has less electrons, and thus the charge state is probably $+3$. In the high spin state, octahedral Co$^{3+}$ has a higher OSPE [45] than Co$^{2+}$. Thus when all Co are made to occupy the octahedral sites as is done in case of $y = 1$, the expected charge state is $+3$. Therefore, the inferences from the features of the densities of states and the crystal field results are consistent. The tetrahedral Mn densities of states are by and large similar to that for $y = 0.5$ signifying that its charge state is insensitive to the degree of cation disorder.

The features in the densities of states for each $y$ can be used to explain the near degeneracy of states (without consideration of entropy) with $y = 0.5$ and $y = 1$ for $x = 0.25$ as is seen in figure 1. A general feature of the densities of states for other compositions is that there is a significant shift of the bands towards higher energies as $y$ changes from 0.5 to 1, explaining the increase in $E_c$ with $y$. This is demonstrated by, for example, appearance of vacant states when $y$ changes from 0.5 to 1 in case of $x = 0.125$. This is not the case for $x = 0.25$ and explains the nearly same $E_c$ for $y = 0.5$ and 1.

One outcome of the systematic explorations of the densities of states is the variations in the nature of the band gap. Since the band gap depends both on the concentration and degree of cation disorder quite substantially (table V, supplementary material), manipulation of the composition and the cation disorder can be a route to engineering band gap in this material which can be subsequently used for applications like solar cells. This widens the functional scope of this material.

4. Summary and conclusions

With density functional theory based techniques, we have investigated the thermodynamics of cation disorder, the structural, the magnetic and the electronic properties of
Co(\text{Cr}_{1-x}\text{Mn})_{x}\text{O}_{4} compounds and analysed the results from their electronic structures and the elements of the crystal field theory. Our results support the model of cation disorder between Co and Mn atoms as proposed by the experimentalists.

The experimental non-regular behaviour of magnetisation as a function of Mn concentration is explained on the basis of that. By generalising a thermodynamic model of cation disorder for \text{AB}_{2}\text{O}_{4} compounds in this case, in conjunction with first-principles total energy calculations, we have quantified the cation disorder parameter for each concentration. Our results have explored the intimate relationships between the degree of cation disorder, the crystal fields associated with different atoms and their charge states, the structural and the magnetic properties.

We have demonstrated that the non-regular behaviour of the magnetic moments and the structural properties can be traced back to the features in their electronic structures. Our results show that the occupancies at the octahedral sites and the associated crystal fields can explain the variations in the properties with varying composition and degree of cation disorder. By calculating the variations in the electronic band gap with variations in composition and degree of cation disorder, we have shown that the functionalities of this material can be enhanced by engineering the band gap through careful manipulation of the composition and the degree of disorder.

Overall, this work has paved a way to compute the thermodynamics of cation disorder in a (\text{AB})_{1-x}\text{C}_{x}\text{O}_{4} magnetic spinel and perform subsequent analysis to understand the microscopic details of such systems. In the context of the specific system considered in this work, our results have provided a robust theoretical background for interpretation of the experimental results.

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