



Role of *p-d* hybridization in structural transition and magnetic properties of Co-substituted Mn_3O_4 : X-ray absorption spectroscopy study

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ABSTRACT

This work investigates the role of *p-d* orbital hybridization in the structural transition from tetragonal $I4_1/amd$ to cubic $Fd\bar{3}m$ and enhancement in Néel temperature (T_N) from 43 K to 175 K in $(\text{Mn}_{1-x}\text{Co}_x)_3\text{O}_4$ (where $x = 0.0, 0.1, 0.2, 0.3, 0.5$, and 0.6). X-ray absorption spectra of Co- $L_{2,3}$ and Mn- $L_{2,3}$ edges show that the high-spin Co^{2+} cations initially substitute the Mn^{2+} at the tetrahedral-sites. When the tetrahedral-sites are fully occupied, then the high-spin Co^{3+} cations begin to occupy the octahedral-site. The substitution of Co cations at both the tetrahedral and octahedral-sites increases the bond angle between adjacent tetrahedral and octahedral site cations via O-2p orbitals, suppressing the orbital instability of Mn^{3+} cations. These effects dramatically enhance the superexchange interaction and hence the T_N .

1. Introduction

Mn_3O_4 is a normal spinel compound where Mn^{2+} cations occupy *Td*-sites while Mn^{3+} occupy *Oh*-sites [1–3]. Mn_3O_4 possesses a cubic $Fd\bar{3}m$ structure above 1443 K but undergoes a structural transition from cubic $Fd\bar{3}m$ to tetragonal $I4_1/amd$ below this temperature [4]. The Mn 3d(e_g) electron of Mn^{3+} in *Oh* crystal symmetry causes an elongation along the *c*-axis by further splitting the 3d orbitals (Jahn-Teller effect), which results in a tetragonal crystal structure. Mn_3O_4 shows a noncollinear ferrimagnetic (Yafet-Kittel type) transition below the Néel temperature 43 K (T_N) [5–8]. Mn_3O_4 exhibits two more magnetic transitions at 39 K and 33 K. The magnetic transition at 39 K appears to be due to the formation of a magnetic spiral phase which is incommensurate with the structural unit cell. Below 33 K, another magnetic transition appears when the incommensurate spiral phase locks into a commensurate spiral phase. Low-temperature structural studies revealed that this commensurate magnetic phase is linked with structural transition from tetragonal to orthorhombic phase below 33 K [9,10]. The cell volume of this orthorhombic unit cell is twice as large as the tetragonal phase (cell-doubled phase) [6]. Spinel systems exhibit various properties such as multiferroicity [11], magneto-dielectric properties [12],

orbital-ordering [13], magnetostriction effect [13–16], magneto-elasticity [17], and noncollinear magnetic ordering [18].

Spinel oxides usually favor cubic crystal symmetry at room temperature [19–26] but a few systems acquire crystal structures with lower symmetry [25,26]. The distorted and geometrically frustrated tetragonal structure of Mn_3O_4 is due to the presence of the Jahn-Teller active Mn^{3+} cation in the *Oh*-site. This crystal structure of Mn_3O_4 is susceptible to coming back to the symmetrical cubic structure if sufficiently large chemical pressure is induced at the *Oh*-site [27]. Here, we investigate the effect of Co-substitution in Mn_3O_4 by studying the structural, magnetic, and electronic structure of the system. The Co-cations are quite interesting as they show multiple valences (+2, +3, and +4) as well as various spin states (low-spin (LS), intermediate-spin (IS) and high-spin (HS) states). Co^{3+} is especially interesting as it could exhibit the LS state ($S=0$, $t_{2g}^6e_g^0$), IS state ($S=1$, $t_{2g}^5e_g^1$), and HS state ($S=2$, $t_{2g}^4e_g^2$) depending on the local environment. The *Td*- and *Oh*-sites of Mn_3O_4 present two different crystal-field environments for substituent Co cations and it is interesting to study the behavior of this system with Co under in these two different crystal field environments. According to our X-ray absorption spectra (XAS) study, Co initially ($x \leq 0.30$) substitutes into the *Td*-site, and then after occupying all the *Td*-sites the remaining

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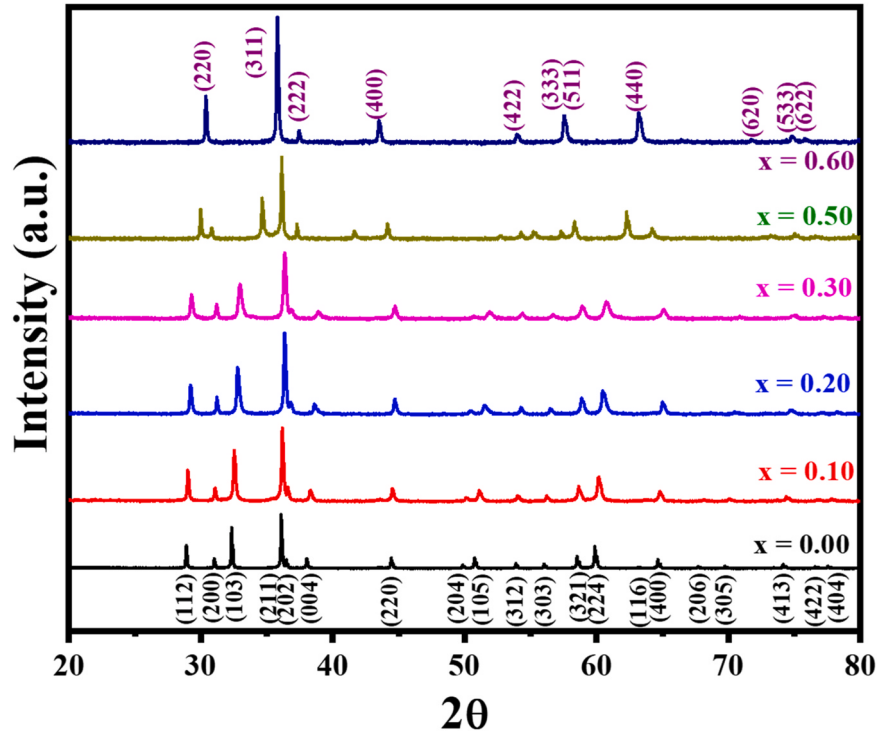


Fig. 1. X-ray diffraction patterns of $(\text{Mn}_{1-x}\text{Co}_x)_3\text{O}_4$ systems (where $x = 0.0, 0.1, 0.2, 0.3, 0.5, \text{ and } 0.6$).

Co cations occupy the *Oh*-sites. It is interesting to note that for $x \leq 0.30$ substitution, there is no significant change in structural parameters, but for $x = 0.5$ the structure parameters sharply change and eventually the system acquires the cubic phase for $x = 0.6$. XAS also revealed that $\text{Co}^{2+/3+}$ cations at *Td/Oh*-sites stay in the HS states (Co^{2+} : $S=3/2$, $e_g^4 t_{2g}^3$, and Co^{3+} : $S=2$, $t_{2g}^4 e_g^2$). Interestingly, we observed a dramatic increase in T_N as Co is introduced into the system. For up to $x = 0.30$ substitution,

the T_N more than doubled from 43 K to 90 K without any structural change. With further increase of Co, for $x = 0.5$ and $x = 0.6$, the T_N shows a sharp jump up to 150 K and 175 K respectively. In this manuscript, we have used X-ray absorption spectroscopy to investigate the electronic structures of Co-substituted Mn_3O_4 to understand the role of O 2p-TM 3d hybridization in the structural transition and enhanced T_N .

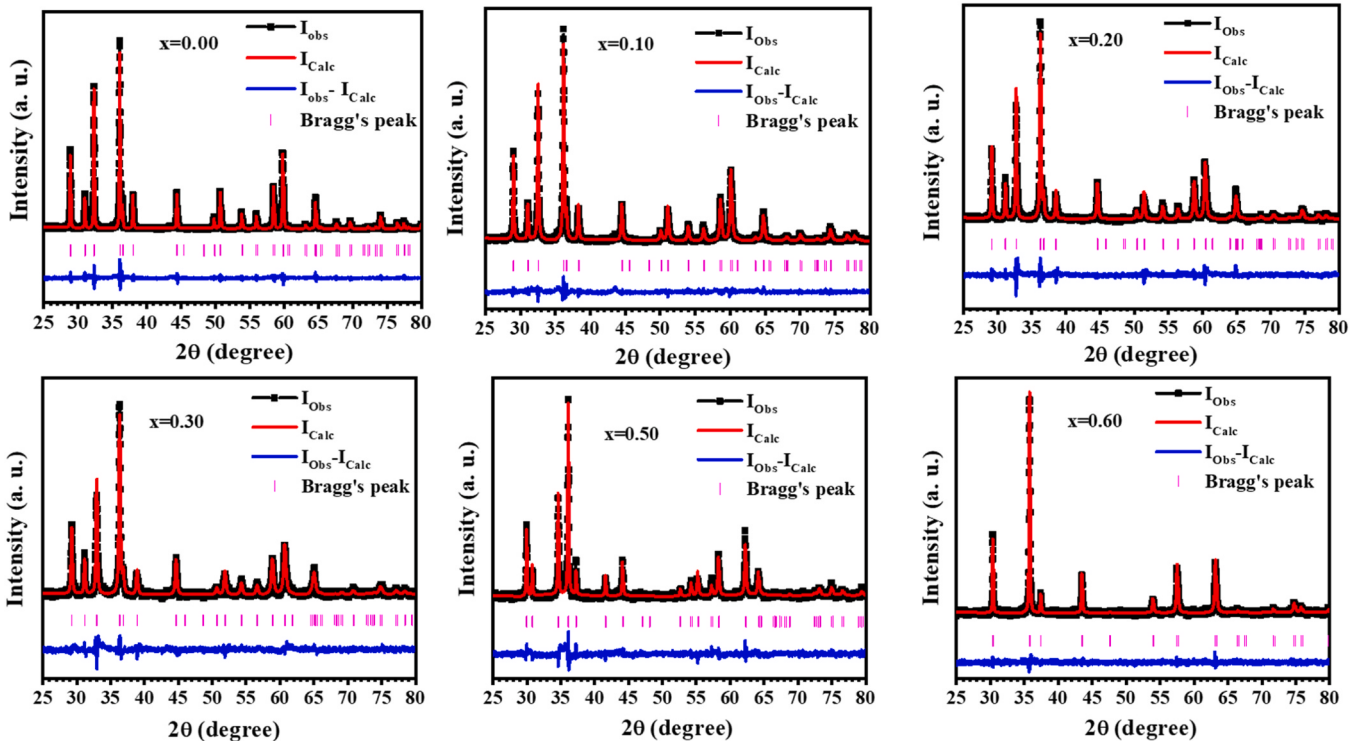


Fig. 2. Refined X-ray diffraction patterns of $x = 0.0, 0.1, 0.2, 0.3, 0.5$ (tetragonal: $I4_1/amd$) and 0.6 (cubic: $Fd\bar{3}m$).

Table 1Summary of the crystal structures, space group, Wyckoff's positions, lattice parameters, and R_p , R_{wp} and χ^2 .

$(\text{Mn}_{1-x}\text{Co}_x)_3\text{O}_4$	Crystal structure, Space group	Wyckoff's position	Lattice parameter (Å)	Goodness of fitting		
				χ^2	R_p	R_{wp}
x = 0.0	Tetragonal, $I4_1/amd$	Mn ²⁺ : 0.00000 0.25000 0.87500 Mn ³⁺ : 0.00000 0.50000 0.50000 O ²⁻ : 0.00000 0.4717(8) 0.2590(8)	a = b = 5.767(9), c = 9.468(1)	1.72	6.07	7.1
x = 0.1	Tetragonal, $I4_1/amd$	Mn ²⁺ /Co ²⁺ : 0.00000 0.25000 0.87500 Mn ³⁺ : 0.00000 0.50000 0.50000 O ²⁻ : 0.00000 0.4738(6) 0.2578(4)	a = b = 5.755(4), c = 9.402(8)	1.51	5.72	6.81
x = 0.2	Tetragonal, $I4_1/amd$	Mn ²⁺ /Co ²⁺ : 0.00000 0.25000 0.87500 Mn ³⁺ : 0.00000 0.50000 0.50000 O ²⁻ : 0.00000 0.4746(1) 0.2579(9)	a = b = 5.742(7), c = 9.334(2)	1.23	3.54	4.63
x = 0.3	Tetragonal, $I4_1/amd$	Mn ²⁺ /Co ²⁺ : 0.00000 0.25000 0.87500 Mn ³⁺ : 0.00000 0.50000 0.50000 O ²⁻ : 0.00000 0.4772(3) 0.2587(1)	a = b = 5.730(9), c = 9.289(5)	1.24	3.06	3.86
x = 0.5	Tetragonal, $I4_1/amd$	Co ²⁺ : 0.00000 0.25000 0.87500 Mn ³⁺ /Co ³⁺ : 0.00000 0.50000 0.50000 O ²⁻ : 0.00000 0.4894(5) 0.2649(6)	a = b = 5.741(1), c = 9.175(5)	1.70	5.12	5.94
x = 0.6	Cubic $Fd\bar{3}m$	Co ²⁺ : 0.12500 0.12500 0.12500 Mn ³⁺ /Co ³⁺ : 0.50000 0.50000 0.50000 O ²⁻ : 0.2610(2) 0.2610(2) 0.2610(2)	a = 8.321(2)	1.09	2.25	2.85

2. Experimental

Polycrystalline $(\text{Mn}_{1-x}\text{Co}_x)_3\text{O}_4$ samples (where x = 0.00, 0.10, 0.20, 0.30, 0.50, and 0.60) were synthesized via the solid-state reaction method. MnO_2 (purity 99.999%, Alfa Aesar) and Co_3O_4 (purity 99.9985%, Alfa Aesar) were mixed in the required stoichiometric ratio and then annealed at 1000 °C for 24 h. Calcined powders were pressed into pellets and annealed again at 1200 °C for 48 h with intermediate grinding. During the final annealing process, the samples were cooled down from 1200 °C to 850 °C at the rate of 5 °C/min, then quenched to room temperature in air. X-ray diffraction patterns were collected with a Bruker D1 diffractometer using $\text{CuK}\alpha_1$ and $\text{CuK}\alpha_2$ with wavelengths 1.54056 Å and 1.54439 Å, respectively. Magnetic measurements were done using a superconducting quantum interference device (SQUID) [Quantum Design Inc.'s Magnetic Property Measurement System XL-7] magnetometer. Mn-L_{2,3}, Co-L_{2,3}, and O-K edge X-ray absorption spectra (XAS) were collected in surface-sensitive total electron yield (TEY) mode at BL20A beamline, National synchrotron radiation research center (NSRRC), Hsinchu, Taiwan. The mean probing depth of TEY mode is ≤ 5 nm for soft X-ray energies [28,29]. The simulations for the Co-L_{2,3} XAS spectra were performed by using an atomic multiplet model including configuration interaction, electron-electron interactions, spin-orbit coupling, crystal field, and hybridization between Co and O [30,31].

3. Results and discussion

3.1. Structural characterization

X-ray diffraction patterns of Co-substituted Mn_3O_4 at room temperature are shown in Fig. 1. Mn_3O_4 crystallizes in a tetragonally distorted $I4_1/amd$ phase which matches well with JCPDS file #240734 and previous reports [27,32,33]. Co-substitution leads all peaks to shift toward a higher angle (viz. lattice contraction) and this trend continues up to a substitution level of x = 0.30. At higher Co concentrations the tetragonal splitting reduces, for example for x = 0.50, and merge for x = 0.60 to attain the cubic crystal structure. Fig. 2 presents the structural refinement results of x = 0.00, 0.10, 0.20, 0.30, 0.50, and 0.60 samples. For x ≤ 0.30, we assume that Mn^{2+} ($r_{\text{Mn}}^{2+} = 0.66$ Å) at the Td -site is replaced with Co^{2+} ($r_{\text{Co}}^{2+} = 0.58$ Å). Due to the smaller ionic radii of Co^{2+} , we observe a slight decrease in lattice constants but we did not observe any structural change in this substitution range. In spinel oxides, one-third of crystallographic sites are Td -site while two-thirds are Oh -sites. Since according to our assumption Co^{2+} is occupying the Td -site, then the Td -sites should be fully occupied by Co^{2+} for x = 0.33 substitution. For substitution levels x = 0.50 and 0.60 the excess Co cations occupy the Oh -site with +3 valence. The replacement of the Mn^{3+} ions by Co^{3+} on the Oh -site reduces the Jahn-Teller distortion and thus the lattice distortion is reduced. Refined lattice parameters of all systems are compiled in Table 1 and Table 2. Previously, we have observed a similar structural transition from tetragonally distorted $I4_1/amd$ to cubic $Fd\bar{3}m$ in Cr-substituted Mn_3O_4 [27]. Fig. 3 presents the crystal structures of x = 0.00, x = 0.30 and x = 0.60 as representative of tetragonal and cubic crystal structures. The crystal structures were

Table 2

Simulated cationic distribution, bond lengths and bond angles of each system are summarized in the table along with their crystal structures.

$(\text{Mn}_{1-x}\text{Co}_x)_3\text{O}_4$	Crystal structure, Space group	Cationic distribution		$\text{TM}_{Td}\text{-O}$ (Å)	$\text{TM}_{Oh}\text{-O}$ (Å)	$\text{TM}_{Oh}\text{-O}_{ap}\text{-TM}_{Td}$ (°)
		Td -site	Oh -site			
x = 0.0	Tetragonal, $I4_1/amd$	Mn^{2+}	Mn^{3+}	$4 \times 2.044(3)$	$4 \times 1.930(2)$ $2 \times 2.288(5)$	124.27(5)
x = 0.1	Tetragonal, $I4_1/amd$	$0.7\text{Mn}^{2+} + 0.3\text{Co}^{2+}$	Mn^{3+}	$4 \times 2.025(8)$	$4 \times 1.930(1)$ $2 \times 2.279(1)$	124.21(7)
x = 0.2	Tetragonal, $I4_1/amd$	$0.4\text{Mn}^{2+} + 0.6\text{Co}^{2+}$	Mn^{3+}	$4 \times 2.021(1)$	$4 \times 1.922(5)$ $2 \times 2.267(2)$	123.82(7)
x = 0.3	Tetragonal, $I4_1/amd$	$0.1\text{Mn}^{2+} + 0.9\text{Co}^{2+}$	Mn^{3+}	$4 \times 2.018(1)$	$4 \times 1.918(8)$ $2 \times 2.238(4)$	123.70(6)
x = 0.5	Tetragonal, $I4_1/amd$	Co^{2+}	$1.5\text{Mn}^{3+} + 0.5\text{Co}^{3+}$	$4 \times 2.009(1)$	$4 \times 1.953(7)$ $2 \times 2.046(5)$	122.97(3)
x = 0.6	Cubic, $Fd\bar{3}m$	Co^{2+}	$1.2\text{Mn}^{3+} + 0.8\text{Co}^{3+}$	$4 \times 1.951(4)$	$6 \times 1.997(7)$	121.75(5)

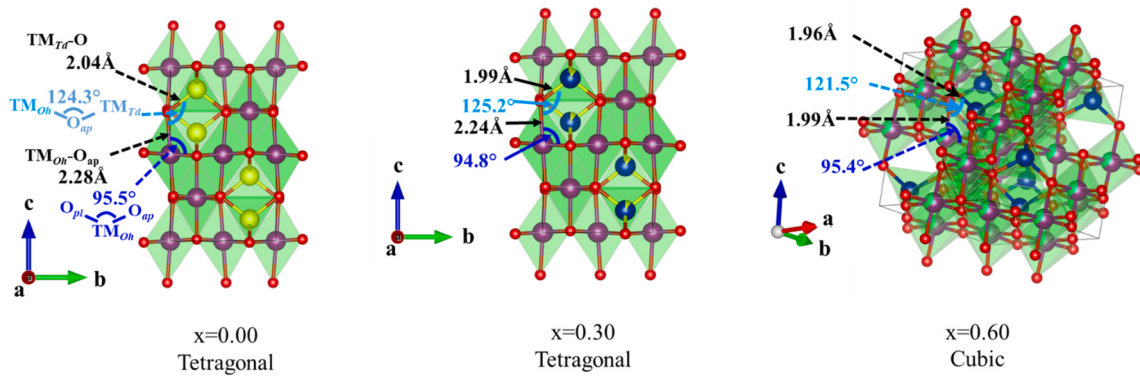


Fig. 3. Crystal structures of tetragonal ($x = 0.0$, $x = 0.3$) and cubic ($x = 0.6$) system constructed with VESTA software [40]. The small red spheres correspond to O²⁻ ion, the yellow spheres correspond to Td-site Mn²⁺ ions, the magenta spheres correspond to Oh-site Mn³⁺ ions, the blue spheres correspond to Td-site Co²⁺ ions and green spheres correspond to Oh-site Co³⁺ ions. The spheres with two colors (in case of $x = 0.30$ and $x = 0.60$) represent the assumption that two ions can occupy the same site.

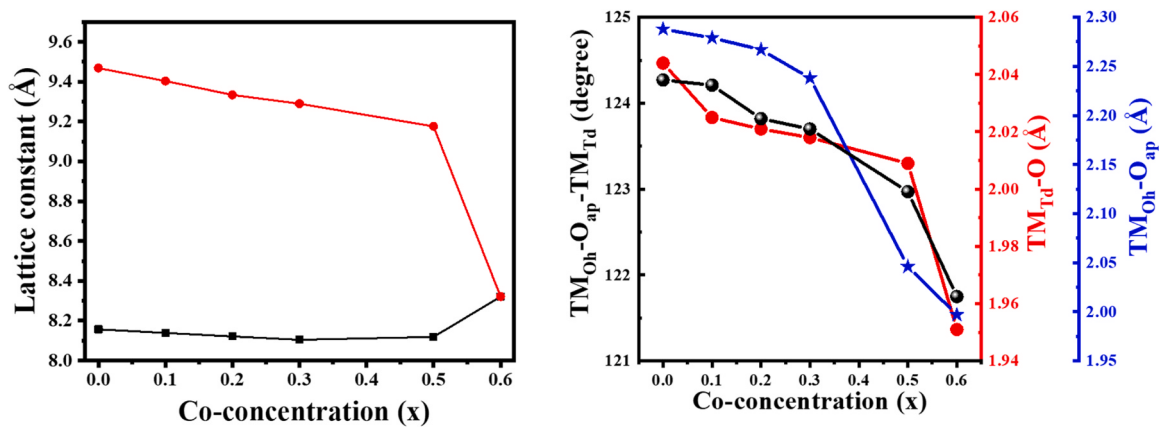


Fig. 4. (a) Lattice parameter as a function of Co-concentration (x). (b) Variation of the bond angle TM_{Oh}-O_{ap}-TM_{Td} and bond lengths TM_{Td}-O, TM_{Oh}-O_{ap}, with respect to Co-concentration (x).

constructed using VESTA software [34]. Fig. 4(a) clearly demonstrates the variation of the lattice constants $a\sqrt{2}$ and c with respect to Co-concentration (x). Fig. 4(b) presents the variations of the TM_{Td}-O bond length, TM_{Oh}-O_{ap} bond length, and the TM_{Oh}-O_{ap}-TM_{Td} bond angle with respect to Co-concentration (x), where TM_{Td} represents the transition metal from Td-site, TM_{Oh} represents transition metal from Oh-site, and O_{ap} represents apical oxygen from Oh-site. When Co is occupying the Td-site, it causes suppression in both TM_{Td}-O and TM_{Oh}-O_{ap} bond lengths while the planar TM_{Oh}-O bond lengths remained almost unchanged around 1.93 Å. The bond lengths and bond angles follow similar trends as shown in Fig. 4(b).

3.2. Magnetic properties

To study the magnetic properties of Co-substituted Mn₃O₄, field-cooled (FC) magnetization vs temperature measurements were done under an applied magnetic field of 25 mT (Fig. 5). Mn₃O₄ shows a ferrimagnetic transition at 43 K, which is consistent with previous reports [27,32]. Interestingly, Co-substitution induces an increase in T_N to 61 K for $x = 0.1$, 77 K for $x = 0.20$, and 90 K for $x = 0.30$. A recently published report has also studied Co-doped Mn₃O₄ up to ~17% i.e.; (Mn_{0.833}Co_{0.167})₃O₄, and they have reported T_N around 62 K for this system [35], which is consistent with our observations. The magnetic interactions of MnCo₂O₄ systems have been studied earlier [36,37], where a number of magnetic interactions are considered depending on various magnetic cations substituting on various sites. Moreover, the

orbital splitting would further increase the active magnetic interactions in the system, which makes the whole scenario much more complicated. Keeping in mind the complexity of this scenario, we will start with a simple approach to understand the magnetic interactions of these systems. Assuming HS Co²⁺ prefers the Td-site, the magnetic interactions between magnetic cations would also change. There are basically three magnetic interactions in spinel systems, (i) Td-Td cations intrasite interaction, (ii) Oh-Oh cations intrasite interaction, and (iii) Td-Oh intersite interactions. The exchange integrals of all these interactions are negative i.e., antiferromagnetic type, where the intersite interaction between Td-Oh cations is strongest [38]. This enforces ferromagnetic alignment of the Td-site spins and Oh-site spins in such a way that they both are aligned antiferromagnetically to each other. However, on the other hand, the coupling between adjacent Oh-sites exhibits a strong competition when they are forced to align in parallel while their intrinsic weak AFM coupling simultaneously intends to drive them away from the parallel alignment. This geometric frustration of the one Td and two Oh-sites substructure gives rise to a noncollinear ferrimagnetic structure, known as Yafet-Kittel type structure. The frustration and Jahn-Teller distortion due to Mn³⁺ cations in Oh-sites lead to a low Néel transition temperature.

Substitution of Co²⁺ at the Td-site affects the Td-Oh interaction more than the Td-Td (and Oh-Oh) interaction which is evident from the observed increase in T_N . For the Td crystal field splitting of TM 3d orbitals, the t_{2g} states acquire a higher energy than the e_g states. The t_{2g} state of Co²⁺ and 3d(t_{2g}/e_g) of Mn³⁺ exhibit a superexchange interaction

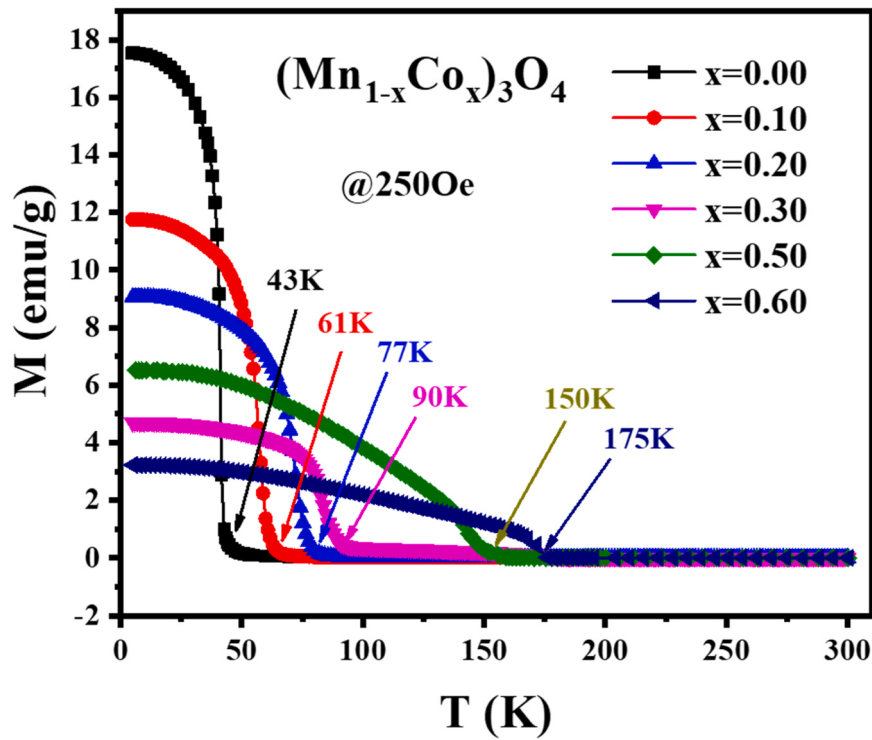


Fig. 5. (a) Field cooled (FC) magnetization vs temperature (M-T) measurements of the $(\text{Mn}_{1-x}\text{Co}_x)_3\text{O}_4$ systems under applied magnetic field of 25 mT. The units of magnetization (emu) and magnetic field (Oe) mentioned in this figure can be converted into SI units using relations; $1 \text{ emu} = 10^{-3} \text{ A}\cdot\text{m}^2$, and $1 \text{ Oe} = (1000/4\pi) \text{ A/m}$.

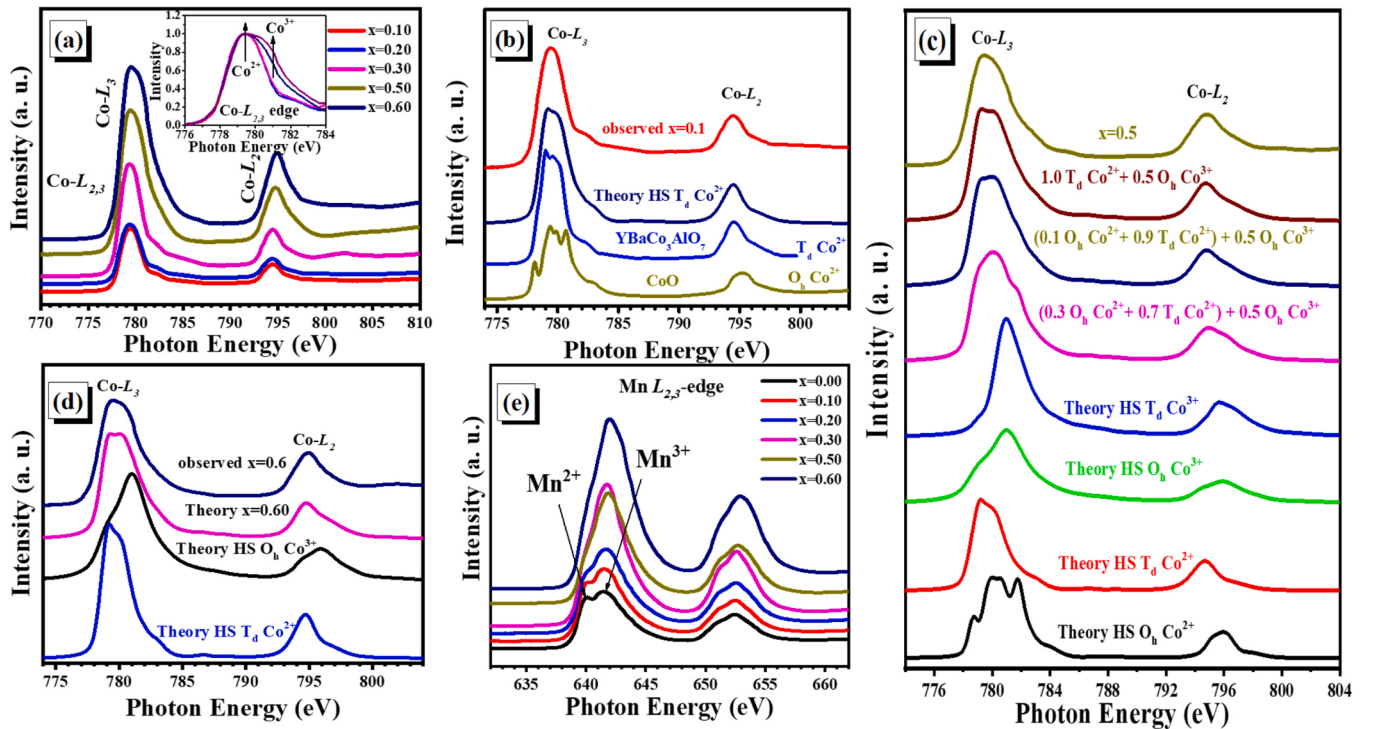


Fig. 6. (a) Comparison of the Co- $L_{2,3}$ edge XAS of $(\text{Mn}_{1-x}\text{Co}_x)_3\text{O}_4$ systems, which shows the emergence of Co^{3+} cation from $x = 0.5$ (inset figure). (b) Comparative study of the Co- $L_{2,3}$ edge of $x = 0.10$ with CoO (*Oh*-symmetry), $\text{YBaCo}_3\text{AlO}_7$ (*Td*-symmetry), and simulated HS Co^{2+} in *Td*-symmetry. (c) Comparison of the Co- $L_{2,3}$ edge spectra for $x = 0.5$ with the theoretical simulations of the Co- $L_{2,3}$ edge spectra assuming normal and inverted cationic distributions under *Td*- and *Oh*- crystal field symmetries with oxidation states (+2 and +3). (d) Comparative study of the Co- $L_{2,3}$ edge for $x = 0.6$ with the simulated HS Co^{2+} at the *Td*-symmetry, simulated HS Co^{3+} in *Oh*-symmetry along with the combination of both simulations assuming a configuration similar to present $x = 0.6$ system. (e) Comparison of the Mn- $L_{2,3}$ edge XAS of $(\text{Mn}_{1-x}\text{Co}_x)_3\text{O}_4$ systems.

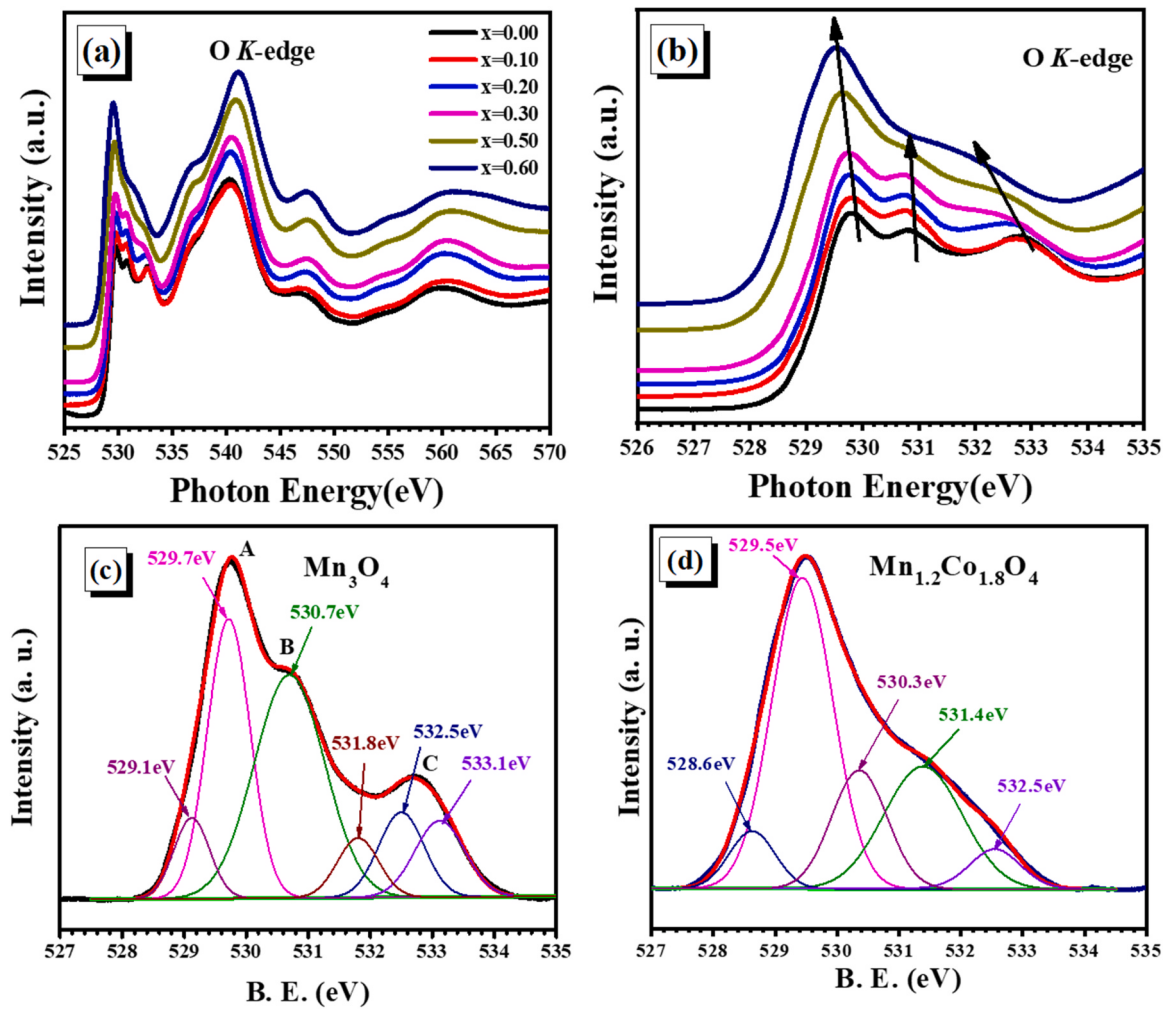


Fig. 7. (a) Comparison of the O-K edge XAS of the $(\text{Mn}_{1-x}\text{Co}_x)_3\text{O}_4$ systems. (b) Enlarged view of the O-K edge in the range 528 eV to 537 eV, featuring hybridized O 2p-TM 3d states. (c) and (d) show the O-K edges of $x = 0.0$ and 0.6 assuming a Jahn-Teller distortion at Oh-site.

via O^{2-} and the electron spins of both cations align antiferromagnetically. According to our structural analysis, we know that substitution of Co cations at the Td -site decreases the $\text{TM}_{Td}\text{-O}$ bond length, $\text{TM}_{Oh}\text{-O}_{ap}$ bond lengths and $\text{TM}_{Oh}\text{-O}_{ap}\text{-TM}_{Td}$ bond angle. As we will discuss in Mn and Co L-edge XAS analysis, all the cations exist in the HS state. This brings us to calculate the individual magnetic moments of cations in the Td - and Oh - sites. At the Td -site, the electronic configuration of Mn^{2+} (d^5) and Co^{2+} (d^7) are $e_g^2 t_{2g}^3$ and $e_g^4 t_{2g}^3$, which results in magnetic moments of $5 \mu_B$ and $3 \mu_B$ respectively. At the Oh -site, the electronic configuration of Mn^{3+} (d^4) and Co^{3+} (d^6) are $t_{2g}^3 e_g^1$ and $t_{2g}^4 e_g^2$, which gives both magnetic moments of $4 \mu_B$. For $x \leq 0.33$ systems, when Co^{2+} occupies Td -site, the average magnetic moment at Oh -site reduces which suppresses magnetic coupling whereas the decrease in bond length and bond angle and the weakened frustration try to increase magnetic interaction. Since the magnetic transition temperature has increased, this suggests that the later effect is dominant in comparison to the first. The presence of Co^{3+} at the Oh -site does not affect the magnetic moment of the Oh -site as Mn^{3+} and Co^{3+} possess same magnetic moment. This means Co^{2+} at the Td -site suppresses the magnetic interaction, while Co^{3+} at the Oh -site does not influence the magnetic interaction. However, the sharp decrease in bond length and bond angle for the $x \geq 0.5$ systems is the origin of the increased magnetic interactions and concomitant just in T_N . According to the Goodenough-Kanamori-Anderson (GKA) rule, these combined changes increase the antiferromagnetic coupling between adjacent TM_{Td} and TM_{Oh} cations. The magnetic transition temperatures of these systems also follow similar

behavior.

3.3. Electronic structure study using XAS

To study the electronic structures of the Co- Mn_3O_4 matrix, we have measured the Co- $L_{2,3}$ edge, Mn- $L_{2,3}$ edge, and O-K edge X-ray absorption spectra of all $(\text{Mn}_{1-x}\text{Co}_x)_3\text{O}_4$ samples in surface sensitive TEY mode. The TM- $L_{2,3}$ edge XAS provides information about the valence band in the vicinity of Fermi-level as it arises due to $2p \rightarrow 3d$ transition. In order to understand the structural behavior of these systems, it is imperative to identify the spin-state of the Co cations and their local geometry in both Td and Oh crystal symmetries. Co- $L_{2,3}$ edge spectra presented in Fig. 6(a) exhibit 2 major structures around 780 eV and 795 eV. These peaks correspond to Co- L_3 and Co- L_2 edges respectively. To compare the valence of Co cations in each system, the Co- $L_{2,3}$ edge XAS spectra were normalized to the intensity of the peak at the Co- L_3 edge (inset Fig. 6(a)). As shown in the inset of Fig. 6(a), the spectra of $x = 0.1, 0.2$, and 0.3 are identical and centered around 779.5 eV while on the other hand, for $x \geq 0.5$, one can observe an increase in the intensity at higher photon energies (~ 781 eV), indicating the presence of mixed valence Co in these systems. Fig. 6(b) compares the Co- $L_{2,3}$ edge X-ray absorption spectra of CoO, $\text{YBaCo}_3\text{AlO}_7$ [39] and the present $x = 0.10$ system. Co^{2+} cations of CoO occupy the Oh -site (dark yellow line), while Co^{2+} cations of $\text{YBaCo}_3\text{AlO}_7$ occupy the Td -site (blue line). We have simulated the Co- $L_{2,3}$ edge XAS curve for low substitution of Co, by assuming HS Co^{2+} cations occupy the Td -site by replacing Mn^{2+} (navy blue). It is clear that

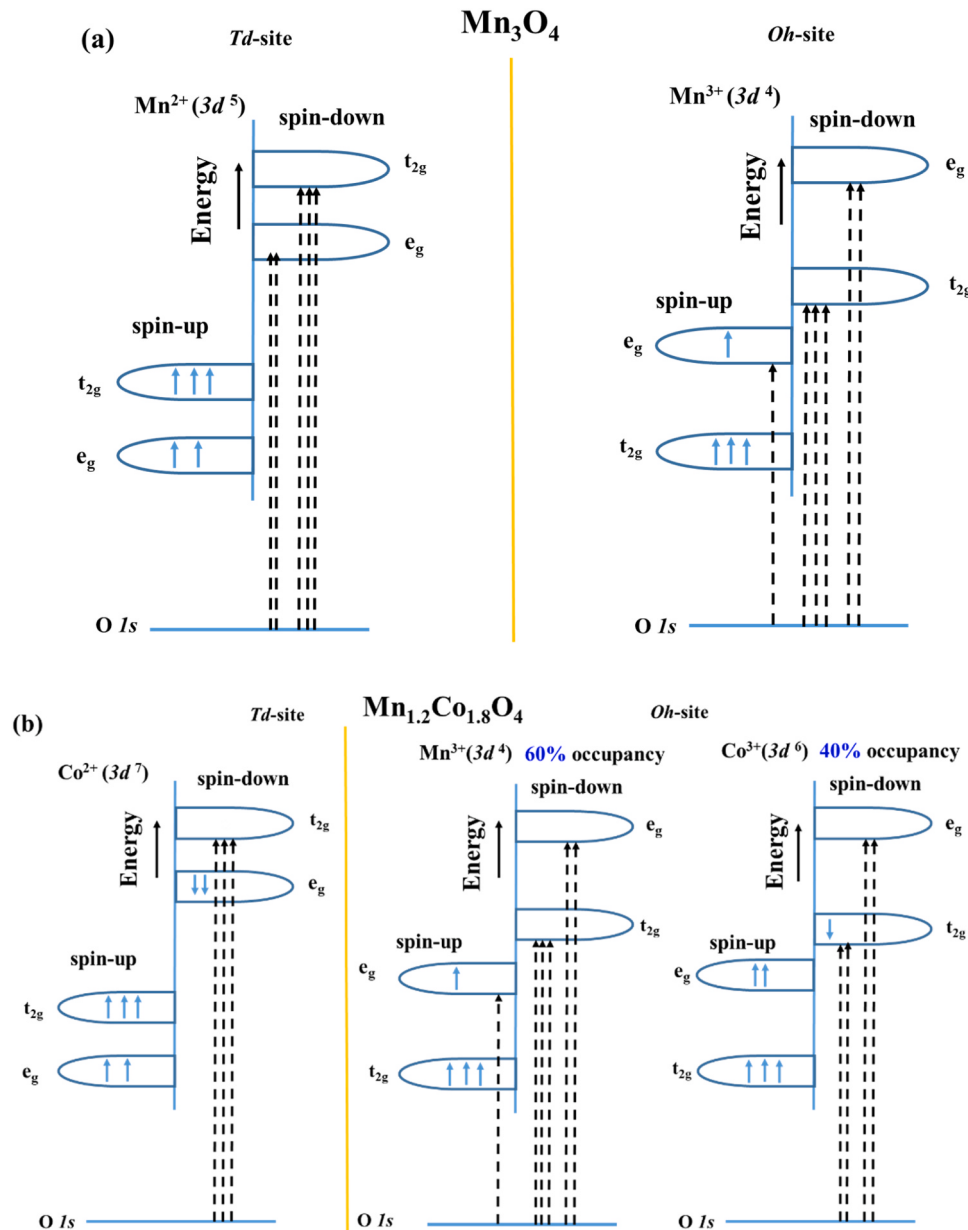


Fig. 8. Schematic diagram of allowed absorption transitions from $\text{O } 1s$ to unoccupied TM $3d$ states of constituent transition metal cations in (a) Mn_3O_4 and (b) $\text{Mn}_{1.2}\text{Co}_{1.8}\text{O}_4$. The dashed arrows represent the allowed transitions to specific orbitals, while the number of arrows to specific orbitals represent the number of unoccupied states in the particular orbitals.

$\text{Co-L}_{2,3}$ edge XAS of $x = 0.10$ matches well with our simulation result as well as the $\text{Co-L}_{2,3}$ edge of $\text{YBaCo}_3\text{AlO}_7$. This $\text{Co-L}_{2,3}$ edge XAS of $x = 0.10$ also confirms that there is no evidence of Co^{2+} at the Oh -site as it would give rise to another structure at higher energy. In Fig. 6(c), we present the $\text{Co-L}_{2,3}$ edge spectra for the $x = 0.5$ system under various conditions. The black and red spectra of the $\text{Co-L}_{2,3}$ edge represent Co^{2+} cations in the high-spin (HS) state at Oh - and Td -sites, respectively. The green and blue spectra of the $\text{Co-L}_{2,3}$ edge represent Co^{3+} cations in the high-spin (HS) state at Oh - and Td -sites, respectively. The magenta and dark yellow spectra of the $\text{Co-L}_{2,3}$ edge represent 30% and 10% of Co^{2+} cations inversely doped into Oh -sites, respectively. The wine spectra of the $\text{Co-L}_{2,3}$ edge represents normal cationic distribution. The navy spectra of the $\text{Co-L}_{2,3}$ edge is the experimental curve of the $x = 0.5$ system. We observed that if we try to include 30% of Co^{2+} at the Oh -site the intensity of the main feature around 779.5 eV reduces and it creates a high-energy shoulder (~ 782 eV). If we try to include only 10% of Co^{2+} at the Oh -site the high energy shoulder still persists with relatively low

intensity. These assumptions do not explain our observed data well. However, the simulation result considering normal cationic distribution, the brown line, does support our experimental data. In Fig. 6(d) we have compared the $\text{Co-L}_{2,3}$ edge spectra of the $x = 0.60$ system with three simulated $\text{Co-L}_{2,3}$ edge XAS curves of (i) HS Co^{2+} cation from Td crystal symmetry (blue line), (ii) HS Co^{3+} cation from Oh crystal symmetry (black line), and (iii) combination of both simulations (magenta line) i. e., Co exists as HS Co^{2+} at the Td -site and as HS Co^{3+} at the Oh -site. The experimental data match well with the third combination simulation curve, consolidating our assumption. These results provide clear evidence that the spinel systems studied in the present work do not exhibit a significant degree of inversion and we can consider them as normal spinel systems. $\text{Mn-L}_{2,3}$ edge spectra consist of two spin-orbit split peaks Mn-L_3 and Mn-L_2 peaks as shown in Fig. 6(e), where two peaks around 640 eV and 642 eV from Mn^{2+} and Mn^{3+} cations originate from the Td - and Oh -sites, respectively. The spectral features match well with reported $\text{Mn-L}_{2,3}$ edge peaks from MnO , MnCr_2O_4 , Mn_3O_4 , Mn_2O_3 , and

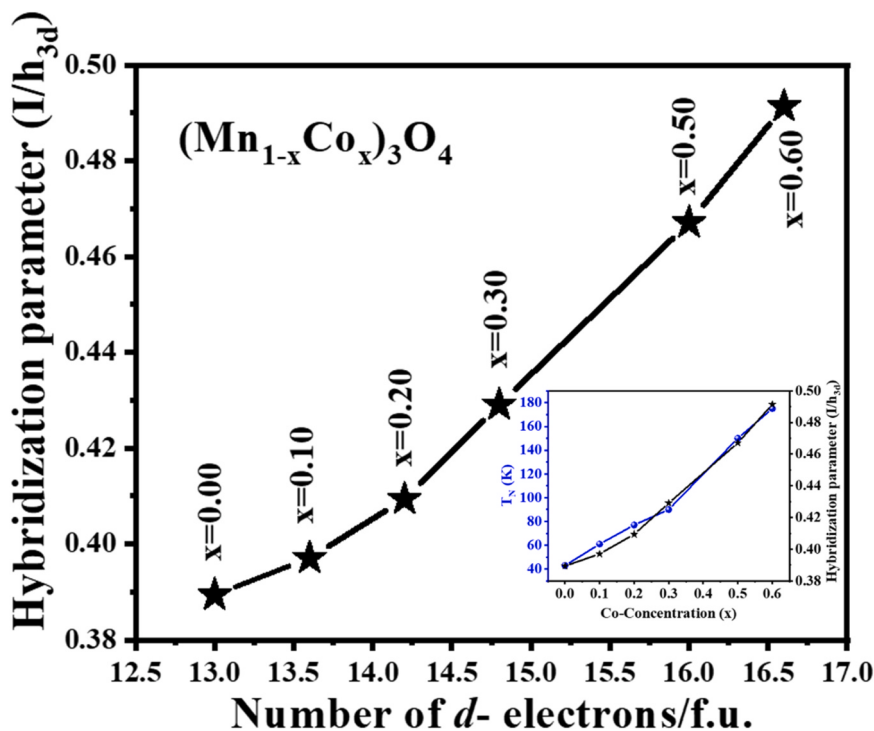


Fig. 9. Variation of the hybridization parameter (I/h_{3d}) with respect to the number of d -electrons per formula unit for these $(\text{Mn}_{1-x}\text{Co}_x)_3\text{O}_4$ systems. Inset figure shows the variation of Néel temperature (T_N) and hybridization parameter as function of Co-concentration.

LaMnO_3 involving Mn^{2+} and Mn^{3+} cations [40–42]. It is clear from the Mn-L_3 peak that with increasing Co substitution the relative peak intensity of Mn^{2+} decreases in comparison to the Mn^{3+} peak intensity. For $x = 0.30$, only the Mn^{3+} peak is clearly observed although a very small structure of Mn^{2+} peak is still present possibly due to presence of 3% Mn^{2+} . For substitution levels $x \geq 0.40$, the Mn^{2+} cations at the Td -site are replaced by Co^{2+} cations and once the all available Td -sites are occupied by Co^{2+} the remaining Co cations replace Mn^{3+} at the Oh -site.

The hybridization between transition metals and oxygen is the key factor in understanding the properties of materials. The O-K edge spectra mainly capture transitions from the O $1s$ state to unoccupied O $2p$ states, hence it provides important information about the degree of hybridization between O $2p$ and TM $3d$ states. Here, TM represents both Mn and Co transition metals. The O-K edge spectra of all Co-substituted Mn_3O_4 are shown in Fig. 7(a), which can be largely divided into two sections. In the first section (528 eV to 534 eV) the oscillations are narrow; while in the second section (>534 eV) the oscillations are broader. The energy range 528 eV–534 eV is attributed to transitions from the O $1s$ to O $2p$ states, which are predominantly hybridized with $3d$ states of transition metals, while the wide peak around 540 eV is attributed to transitions from the O $1s$ to O $2p$ states hybridized with $4s$ and $4p$ states of transition metals [43–45]. The broader spectral shapes, in the second section, largely remain unchanged throughout the entire substitution range, except a slight shift of peaks towards higher energy. Since the bandwidth of the $4sp$ states is wide, the small change in ionic radii of Co and Mn cations would not affect their hybridization with O $2p$, hence these spectral features largely remain unchanged. Contrary to the second section, peaks of the first section exhibit a significant change in spectral features with Co-substitution. To have a closer look at narrow oscillations in the first section, an enlarged view of the 526 eV to 535 eV region is shown in Fig. 7(b). There are three distinguishable peaks around 529.8 eV (peak A), 530.7 eV (peak B), and 532.8 eV (peak C) for Mn_3O_4 within the above-mentioned range. The $3d$ states of the transition metal cations situated at Td -sites and Oh -sites hybridize with O $2p$ states and contribute to these spectral features. Here, we try to understand the origin of all the O-K edge XAS peaks of Mn_3O_4 by considering all possible

transitions from Td -site and Oh -site cations. Mn^{2+} present at the Td -site should give rise to 2 transitions, O $1s$ to TM $3d(e_g\downarrow)$ and to TM $3d(t_{2g}\downarrow)$, while Mn^{3+} at 2 separate Oh -sites should give rise to 3 transitions O $1s$ to TM $3d(e_g\uparrow)$, to TM $3d(t_{2g}\downarrow)$, and to TM $3d(e_g\downarrow)$ (Fig. 8(a)). In total, we should observe 5 peaks. Since the XAS spectra present only three peaks, it shows that all allowed transitions do not form distinct peaks but merge to form three broader peaks. We have fit the 527 eV to 535 eV region of the O-K edge XAS by considering all 5 possible transition discussed above. Moreover, we have added one more peak due to the Jahn-Teller distortion, which causes a further splitting of e_g states into d_{3z}^2 and d_{xy}^2 states. The six-peak model provides a satisfactory fitting result of XAS curve (Fig. 7(c)). Mn cations exhibit Oh crystal-field splitting energy (Δ_{Oh}) of around 3 eV between t_{2g} and e_g states [41,45–47], while the Td crystal-field splitting energy (Δ_{Td}) is $\frac{4}{9} \times \Delta_{Oh}$ i.e., around 1.3 eV. Peak A can be fit with two peaks at 529.1 eV and 529.7 eV, where the 529.1 eV peak corresponds to O $1s$ to $\text{TM}_{Oh} 3d(e_g\uparrow)$ while the 529.7 eV peak corresponds to O $1s$ to $\text{TM}_{Oh} 3d(t_{2g}\downarrow)$ of the Oh -site. Peak B consists of two peaks at 530.7 eV and 531.8 eV, corresponding to transitions from O $1s$ to $\text{TM}_{Td} 3d(e_g\downarrow)$ and O $1s$ to $\text{TM}_{Td} 3d(t_{2g}\downarrow)$ with separation around 1.1 eV. The peak C at 532.7 eV is further split into two peaks around 532.5 eV and 533.1 eV corresponding to d_{3z}^2 and d_{xy}^2 states. The peaks around 529.7 eV and 532.5 eV correspond to O $1s$ to $\text{TM}_{Oh} 3d(t_{2g}\downarrow)$ and O $1s$ to $\text{TM}_{Oh} 3d(e_g\downarrow)$ respectively, which is 2.8 eV apart. Similarly, the O-K edge XAS of cubic $(\text{Mn}_{0.4}\text{Co}_{0.6})_3\text{O}_4$ also has been analyzed. Inclusion of Co^{2+} at the Td -site and Co^{3+} at the Oh -site reduces the probability of most of the absorption transitions as shown in Fig. 8(b). The peak around 528.6 eV corresponds to O $1s$ to $\text{TM}_{Oh} 3d(e_g\uparrow)$. The peaks around 529.5 eV and 532.5 eV arise from the O $1s$ to $\text{TM}_{Oh} 3d(t_{2g}\downarrow)$ and O $1s$ to $\text{TM}_{Oh} 3d(e_g\downarrow)$ transitions, respectively. The peaks around 530.3 eV and 531.4 eV correspond to transitions from the O $1s$ to Td crystal-field split $\text{TM}_{Td} 3d(e_g\downarrow)$ and $\text{TM}_{Td} 3d(t_{2g}\downarrow)$ states (Fig. 7(d)). The most interesting observation in the O-K edge XAS of cubic $(\text{Mn}_{0.4}\text{Co}_{0.6})_3\text{O}_4$ is the absence of a significant Jahn-Teller distortion. The peak around 532.5 eV corresponding to TM $3d(e_g\downarrow)$ does not show significant splitting.

Jin Suntivich, et al. [48] have carried out an extensive study on the

O-K edge absorption spectra of various transition metal systems and they observed that the O 2p-TM 3d hybridization increases with increasing number of 3d electrons as well as with oxidation number. The O 2p-TM 3d hybridization is proportional to the intensity of the 2p-3d excitation and reciprocal to unoccupied 3d-electrons, i.e.; hybridization parameter (H) is proportional to I/h_{3d} where we have defined I as background-corrected intensity of the 2p-3d excitation, and h_{3d} is the total number of unoccupied 3d states. Substitution of Co cations does not affect the oxidation state of transition metal cations (Co^{2+} and Co^{3+} cations replace Mn^{2+} and Mn^{3+} cations), but it increases the number of d-electrons in the system. This increased number of 3d electrons would increase the hybridization between O 2p and TM 3d states. We have plotted the variation of hybridization parameter (H) with respect to the number of 3d electrons per formula unit in our systems (Fig. 9). The hybridization parameter increases with increasing number of 3d electrons in the system. Hence, our results also coincide with the conclusions of Jin Suntivich *et al.* [48]. Combination of these results indicate that Co-substitution enhances hybridization between the O 2p and TM 3d states and tries to bring all hybridized states towards equal energy level i.e., Co-substitution leads the system towards higher symmetry. The electronic local function graph can also be used to get an intuitive idea about the hybridization in the system as reported by Wang *et al.* [49]. But, the hybridization parameter (H) estimated using present method provides a satisfactory correlation with Néel temperature (T_N). Inset Fig. 9 shows H and T_N vary similarly with respect to the Co-concentration in the system. This shows that the hybridization parameter estimated from this method provides a satisfactory picture of the magnetic interactions in these systems.

4. Conclusions

We observed a room temperature structural transition from tetragonal $I4_1/amd$ to cubic $Fd\bar{3}m$ along with a dramatic increase in T_N from 43 K to 175 K in the Co-substituted Mn_3O_4 system. Mn-L_{2,3} edge and Co-L_{2,3} edge XAS revealed that Mn^{2+} cations at the Td-sites are replaced by HS Co^{2+} cations and Mn^{3+} cations at the Oh-site are replaced by HS Co^{3+} cations. The O-K edge XAS showed that the incorporation of Co strengthens the hybridization between O 2p-TM 3d. This increased 2p-3d hybridization increases the symmetry by lowering the energy gap between all hybridized states. Moreover, the increased hybridization also supports the superexchange interaction between magnetic cations which in turn increases T_N .

CRedit authorship contribution statement

G.D. Dwivedi: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft, Writing – review & editing. **S.M. Kumawat:** Data curation. **Y.Y. Chin:** Methodology. **J.W. Lynn:** Writing – review & editing. **H. Chou:** Conceptualization, Formal analysis, Funding acquisition, Resources, Supervision, Visualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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