

## DIFFERENT DOPANT RELATED TO MAGNETIC ORDER AND LOCAL STRUCTURAL CHANGES IN SrYCoO<sub>3</sub> BASED COMPOUND

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*A study is conducted on the relation between dopant induced changes in magnetic properties and local structural modifications in Sr<sub>0.775</sub>Y<sub>0.225</sub>(Co<sub>0.9</sub>Zn<sub>0.1</sub>)O<sub>3-δ</sub>. Temperature and field dependent magnetic responses of this compound are found to differ from those previously reported for Sr<sub>0.775</sub>Y<sub>0.225</sub>(Co<sub>0.9</sub>Fe<sub>0.1</sub>)O<sub>3-δ</sub>. The Fe-doped compound show near total suppression of FM, while Zn-doped compound retain measurable FM ordering. Local structures are shown to exhibit perceptible differences of Co-O bond lengths and Co-O-Co bond angles in the fully oxygenated octahedral layer. Those differences are argued to result in the different CF strengths that affect differently the Co<sup>3+</sup> spin states and the inter-ionic magnetic interactions.*

**Keywords:** Co-based perovskite compounds: Sr<sub>0.775</sub>Y<sub>0.225</sub>(Co<sub>0.9</sub>TM<sub>0.1</sub>)O<sub>3-δ</sub> (TM = Fe, Zn); Co<sup>3+</sup> spin states, ferromagnetic and antiferromagnetic orderings; doping induced effects; magnetic and local structural correlation.

### 1. Introduction

The cobalt based oxides that belong to the strongly correlated electron systems have been the subject of numerous studies owing to the wide ranging dopant induced novel phenomena and useful properties exhibited by these materials. Well known among them are room temperature superconductivity, thermoelectricity, multiferroism, ionic conductivity, magnetic transition and insulator–metal transition (IMT), as well as magnetoresistivity (MR) [1]. This rich functional versatility is related with the large variety of cobalt valence states of Co<sup>2+</sup>, Co<sup>3+</sup>, Co<sup>4+</sup> and a mixed valence state in the surrounding environment of oxygen anions, depending on the dopant introduced and the resulted content of

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oxygen vacancy. Besides, its coordination with the oxygen atoms can stabilize the compound in local structures of different geometries, such as tetrahedral, pyramidal, and octahedral coordinations. Further, a special property that distinguishes the cobalt oxide from most other 3d metal oxides is its possibility to have various spin states of the Co ion, covering the low spin (LS), high spin (HS), and intermediate spin (IS) states. These different states are known to be closely related with the different magnetic properties of the compounds and they have their origins in the different competitions between the crystal field (CF) induced  $e_g-t_{2g}$  splitting energy  $\Delta_{CF}$  and the Hund's energy of intra-atomic spin-spin coupling. The magnitude and nature of crystal field splitting together with the  $\text{Co}^{3+}$  spin state in turn depends sensitively on the Co-O bond length, and the local symmetry, while the Co-O-Co bond angle may influence the magnetic interaction between the magnetic ions. Spin state transition temperatures as well as magnetic responses of the compounds can therefore be readily affected by changing the local structure induced by varying the temperature, pressure, or magnetic field applied to the crystal. Among the most intensively studied subjects are however, the effects induced by changing the oxygen content or partial substitutions of the cations in the crystal.

The single crystal  $\text{SrCoO}_3$  compound first synthesized in 2011 was shown [2] to be a cubic perovskite system that stabilized to the crystal structure of  $Pm\bar{3}m$  space group. Intensive studies conducted subsequently [2] on the single crystal samples further showed that this system exhibited an itinerant ferromagnetic behavior with a Curie temperature of 305 K. Its easy magnetization axis was found to be along the [111] direction with a saturation moment of about  $2.5 \mu_B/\text{f.u.}$  in its ground state, in agreement with the IS state of  $\text{Co}^{4+}$  ions as predicted theoretically [3], [4]. Doping of the  $\text{SrCoO}_3$  on either the Sr or Co site is known to result in fractional valences of Co ions along with non-stoichiometric oxygen content [5], [6], [7]. In particular, the judiciously doped compounds have been shown to acquire novel and useful functional properties not available in their undoped parent compound [8].

Specifically, the  $\text{SrCoO}_3$  system doped with Ln (Ln = Y or a rare-earth element) on the Sr site is known to yield the  $\text{Sr}_{1-x}\text{Ln}_x\text{CoO}_{3-\delta}$  system that stabilizes in an A-site ordered and distorted perovskite structure [9], [10], [11], [12]. The Y doped compounds have been widely reported to result in the structural change from cubic into tetragonal crystal with  $I4/mmm$  space group in conjunction with the occurrence of bulk ferromagnetic signal in the narrow dopant range of  $0.20 \leq x \leq 0.25$  [6], [13], with the highest ferromagnetic ordering temperature of  $T_C \cong 335$  K observed for  $x = 0.225$  and  $\delta \approx 0.35$ , irrespective of the Ln dopant used [6]. On the other hand, the  $\text{Sr}_{2/3}\text{Y}_{1/3}\text{CoO}_{3-\delta}$  compound at  $\delta = 0$  which is known as an antiferromagnetic insulator with  $T_N = 290$  K, was reported to go over to ferromagnetic compound at  $T_C = 225$  K with a subtle increase of the oxygen

deficiency of  $\delta = 0.04$  in conjunction with the slight change in the oxidation state of the cobalt ions [14]. The Co-ions in this system are known to occupy two different sublattice sites with Co1 occupying the oxygen deficient tetrahedral CoO<sub>4+ $\delta$</sub>  layer and the Co2 residing in the fully oxygenated octahedral CoO<sub>6</sub> layer with lower magnetic moment. The origin of ferromagnetic component had nevertheless been an issue of prolong controversies [6], [15], [16], [17], [18], [19], [20]. It is only recently, a comprehensive and detailed study [21] on the basis of data obtained by scanning transmission electron microscopy (STEM)-annular bright field (ABF) imaging technique, combined with density functional theory (DFT) calculation, succeeded to show that the observed ferromagnetism mainly arises from the fully oxygenated CoO<sub>6</sub> octahedral layers where the Co<sup>3+</sup> ions are antiferromagnetically aligned with alternating high spin and intermediate spin resulting in ferrimagnetism. The oxygen deficient tetrahedral CoO<sub>4+ $\delta$</sub>  layers, on the other hand, consist mainly of high spin Co<sup>3+</sup> ions aligned antiferromagnetically within the layer. The study implies the different structural origins of the different magnetic responses.

Since the magnetism of SrCoO<sub>3- $\delta$</sub>  system is largely determined by the magnetic character of Co ions in coordination with the surrounding oxygens, it is understood that Sr<sub>1-x</sub>Ln<sub>x</sub>CoO<sub>3- $\delta$</sub>  has relatively robust magnetic ordering against the change of Ln dopant [6], [7]. In the contrary, the magnetic property of this system was shown to be susceptible to the partial substitutions of Co by different dopants [22], [23], [24], [25]. In particular, it was reported that 25% substitution of Co with non-magnetic Ga in the Sr<sub>0.75</sub>Y<sub>0.25</sub>CoO<sub>3- $\delta$</sub>  only resulted in significantly reduced ferromagnetic order and lowering of its transition temperature from 320 K for Sr<sub>0.7</sub>Y<sub>0.3</sub>CoO<sub>2.62</sub> to 225 K for Sr<sub>0.75</sub>Y<sub>0.25</sub>Co<sub>0.75</sub>Ga<sub>0.25</sub>O<sub>2.625</sub> [22]. On the other hand, even with relatively small (10-12%) Co substitution by the magnetic Fe dopant, the system was already reported to suffer from largely suppressed ferromagnetic signal in conjunction with dominant appearance of antiferromagnetic component at almost the same transition temperature,  $T_N \cong 350$  K [23], [24], [25]. Meanwhile measurable structural changes in terms of thickness changes in the tetrahedral and octahedral block layers were also reported in connection with the decrease of oxygen deficiency, both of which were suggested to be related with the weakened ferromagnetic order [25].

In this study an attempt is made to analyze and relate the non-magnetic dopant induced changes in magnetic behaviors of Sr<sub>0.775</sub>Y<sub>0.225</sub>Co<sub>0.9</sub>Zn<sub>0.1</sub>O<sub>3- $\delta$</sub>  with the corresponding modifications of its local structure. The result are compared with previously reported data for the solely Y doped SrCoO<sub>3</sub> compound Sr<sub>0.775</sub>Y<sub>0.225</sub>CoO<sub>3- $\delta$</sub>  (hereafter abbreviated as SYCO) and the compound with additional Fe doping cited earlier [25]. The different local structural changes are further analyzed for their possible different effects on the crystal fields around the associated Co<sup>3+</sup> and Fe<sup>3+</sup> ions, leading to related changes of their spin states.

Those structural changes may also influence the inter-ionic distances and thereby affect the magnetic interaction between the nearby magnetic ions. Together these structure related effects are expected to provide a plausible explanation on the observed different magnetic behaviors of the differently doped compounds.

## 2. Experimental

The powder sample of  $\text{Sr}_{0.775}\text{Y}_{0.225}(\text{Co}_{0.9}\text{Zn}_{0.1})\text{O}_{3-\delta}$  is synthesized by means of the standard solid-state reaction method. The starting materials consisting of  $\text{SrCO}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$ , and  $\text{ZnO}$  compounds are provided by Sigma Aldrich with better than 99.9% purity. The mixture is prepared according to the stoichiometric formula with thorough grinding and mixing before being pelletized for calcination at  $1000^\circ\text{C}$  for 10 hours. This is followed by the sintering process at  $1100^\circ\text{C}$  for 20 hours in air which is interrupted with intermediate grindings. The resulted sample is furnace cooled.

The DC magnetization measurements are performed with a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS). The temperature dependent magnetization ( $M$ - $T$  curve) measurements are performed in an applied  $H$  field of 1 kOe. The field dependent magnetization ( $M$ - $H$  curve) is measured in  $H$  up to 70 kOe at 10 K. The structural characterization of the sample is performed by means of X-ray diffraction (XRD) measurement using Philips machine with  $\text{Cu-K}\alpha$  radiation source. The data are taken for diffraction angle ( $2\theta$ ) ranging from  $10^\circ$  to  $110^\circ$ , at a step of  $0.02^\circ$ . Refinement analysis of the XRD patterns is carried out according to Rietveld method [26].

## 3. Results and Discussion

### A. Results of Magnetization Measurements

The  $M$ - $T$  curve of the Zn doped  $\text{Sr}_{0.775}\text{Y}_{0.225}(\text{Co}_{0.9}\text{Zn}_{0.1})\text{O}_{3-\delta}$  sample measured in an applied field of  $H = 1000$  Oe and the  $M$ - $H$  curve measured at  $T = 10$  K are presented in Figs. 1 (a) and (b), respectively. The corresponding data for  $\text{Sr}_{0.775}\text{Y}_{0.225}(\text{Co}_{0.9}\text{Fe}_{0.1})\text{O}_{3-\delta}$  compound reported previously [25] are also reproduced in Figs. 1 (c) and (d) for easy comparison. It is shown that 10% substitution of Co with either transition metal (TM) element results in considerably reduced magnetization values compared with the result reported for  $\text{Sr}_{0.775}\text{Y}_{0.225}\text{CoO}_{3-\delta}$  (SYCO) [25] which will be presented and discussed later, although the magnetic transition temperatures remain relatively less affected, namely about  $T = 350$  K for Fe-doped and  $T = 330$  K for Zn-doped compound compared to 340K for SYCO [25]. One further notices that the Fe and Zn-doped

samples exhibit some different features in the M-T curves, but the more remarkable difference is however depicted by Fig. 1 where the near total suppression of FM signal is indicated by the straight M-H line at 5K shown in Fig. 1(d). On the other hand, one notes the appearance of small but perceptible ferromagnetic signal (hysteresis loop) in Fig. 1(b) for Zn-doped compound, which is characterized by a remanence magnetization of  $M_r \sim 0.11\mu_B$  per Co ion and a coercive field  $H_c$  of about 4.39 kOe, even at a higher temperature of 10 K. These different magnetic responses induced by the two TM dopants will be further related with the corresponding local structures in the next subsection.

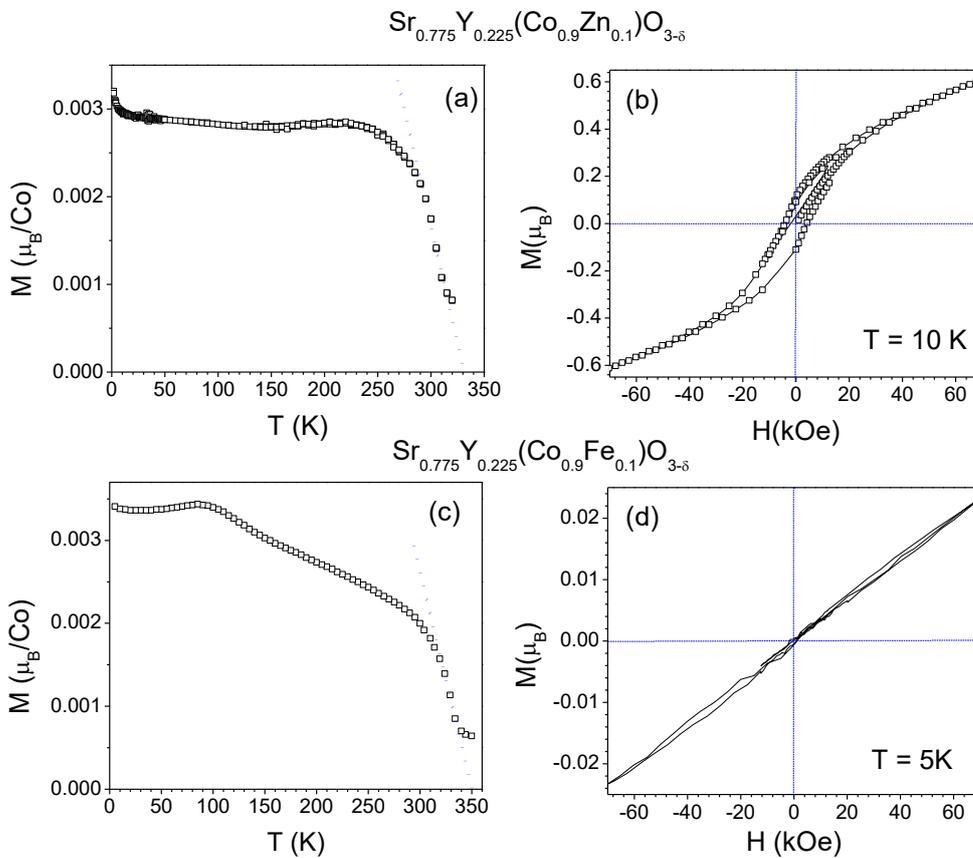


Fig. 1. The temperature and field dependent magnetization curves measured from  $\text{Sr}_{0.775}\text{Y}_{0.225}(\text{Co}_{0.9}\text{TM}_{0.1})\text{O}_{3-\delta}$  for TM = Zn (a,b) and those of TM = Fe (c,d) reproduced from reference [25]. The thin dotted lines in (a) and (c) are the linear extrapolations of the high temperature M-T data for indicating the onset temperatures of the corresponding transitions at 330K and 350K, respectively. Note the different scales used in the two M-H curves.

Since the two compounds discussed above can be regarded as having the same “mother” compound of SYCO, it will be useful to compare the different magnetic behaviors induced by the different extra dopants in comparison with their “mother” compound. The M-T curves measured in  $H = 1000$  Oe together with the M-H curve measured at  $T = 2$  K from this compound are reproduced from reference [25] in Figs. 2(a) and (b), respectively. It is seen that the M-T curves displayed in Fig. 2(a) clearly shows the magnetic transition occurring at roughly the same temperature as reported previously [5], [13]. Meanwhile the M-H curve in Fig. 2(b) does exhibit an undisputable hysteresis sign, although it is marked by a rather small remanence magnetization of  $M_r < \sim 0.15 \mu_B$  per Co ion and a coercive field  $H_c$  of about 16 kOe which is significantly larger than the values cited for the Zn-doped sample. As mentioned earlier, the magnetization value in this case is almost one order of magnitude larger, confirming the more sensitive effect of Co substitution by other elements mentioned earlier. It is important to note, while the introduction of magnetic Fe dopant in the SYCO compound suppresses its FM signal, the same amount of non-magnetic Zn doping clearly fails to eliminate the hysteretic signal. It is obvious that this remarkable difference do not have much to do with the magnetic properties of the dopants involved. It is therefore desirable to seek the possible clues in the different changes of local structures caused by the two TM dopants.

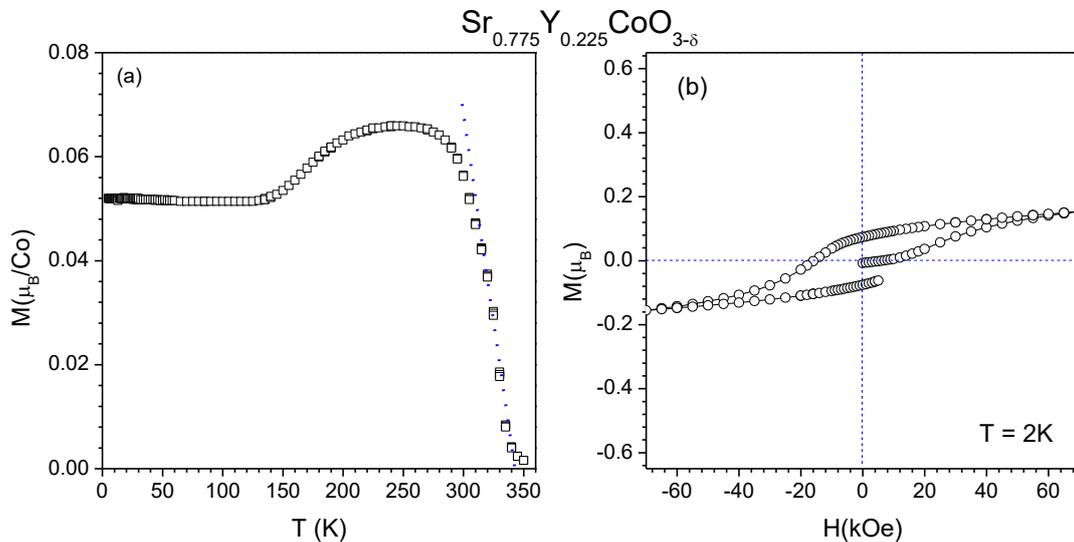


Fig. 2. (a) The temperature dependent magnetization curve of  $\text{Sr}_{0.775}\text{Y}_{0.225}\text{CoO}_{3.8}$  measured at  $H = 1000$  Oe and (b) M-H curve measured at  $T = 2$  K which are reproduced from [25] for comparison with Fig. 1. The straight line in (a) is the linear extrapolations of the high temperature data for indicating the onset temperature of 340K for the magnetic transition.

## B. Dopant Induced Structural Changes

In order to reveal the dopant induced structural changes in the Zn doped sample, the associated XRD pattern is refined by adopting the space group of *I4/mmm* for tetragonal crystal structure. Further, the Zn dopants in the refinement model are supposed to be distributed evenly on the two separate sublattice sites of different oxygen coordinations as previously adopted for Fe doped compounds [22], [23], [24], [25]. Listed in Table 1 are the best fitted lattice parameters together with the tetragonal distortion indices of the unit cell as measured by the  $c/2a$  ratio. The results reported in Ref. [25] are also included in the table for comparison.

Table 1

**The lattice parameters and tetragonal distortion indices of the unit cells obtained from refinement of the XRD data of Sr<sub>0.775</sub>Y<sub>0.225</sub>CoO<sub>3-δ</sub> and Sr<sub>0.775</sub>Y<sub>0.225</sub>(Co<sub>0.9</sub>TM<sub>0.1</sub>)O<sub>3-δ</sub> (TM = Fe, Zn) compounds. Data of the compounds marked by (\*) are taken from Ref. [25].**

Compound	Lattice parameters (Å)		$c/2a$
	$a$	$c$	
Sr <sub>0.775</sub> Y <sub>0.225</sub> CoO <sub>3-δ</sub> (*)	7.655	15.353	1.00278
Sr <sub>0.775</sub> Y <sub>0.225</sub> (Co <sub>0.9</sub> Fe <sub>0.1</sub> )O <sub>3-δ</sub> (*)	7.649	15.358	1.00392
Sr <sub>0.775</sub> Y <sub>0.225</sub> (Co <sub>0.9</sub> Zn <sub>0.1</sub> )O <sub>3-δ</sub>	7.667	15.358	1.00330

It is seen from the table that the additional doping with either Fe or Zn dopant increases the tetragonal distortion indicated by the enlarged  $c/2a$  indices. On the other hand, the  $c$  lattice parameters in the samples with the additional TM dopants appears relatively unchanged with respect to that of SYCO sample. Meanwhile considerable differences in  $c/2a$  are found among the three compounds. In particular, the largest  $a$  parameter is found in the Zn doped compound, which may be attributed to the largest ionic radius of Zn<sup>2+</sup> ion compared to those of Co<sup>3+</sup> and Fe<sup>3+</sup> ion. The significance of these differences will be further elucidated in terms of the corresponding local structural differences.

For this purpose, it is helpful to present in Fig. 3 the basic crystal structure of SYCO generated using the Vesta program [27]. The structure displays alternate stacks of oxygen deficient tetrahedral CoO<sub>4+δ</sub> layers containing Co1 cations and the fully oxygenated octahedral CoO<sub>6</sub> layers occupied by Co2 cations. As suggested recently [28], the dopant induced structural modifications in these two layers are similar to the effect of external physical pressure which are supposed to

have major influences on magnetic behaviors of the corresponding compound, corroborating the conclusion given in Ref. [21].

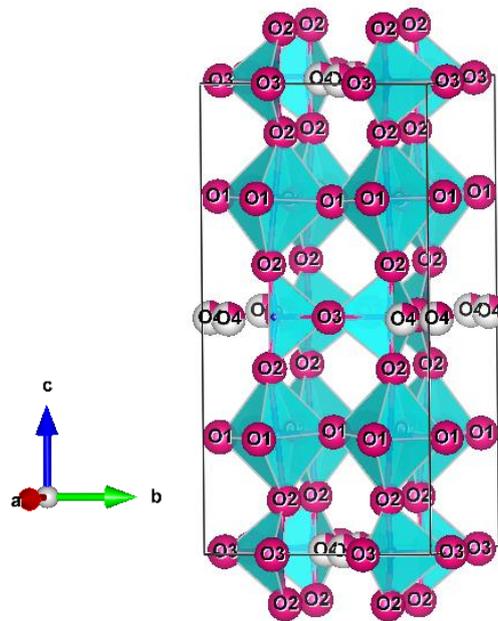


Fig. 3. The crystal structure of  $\text{Sr}_{0.775}\text{Y}_{0.225}\text{CoO}_{3-\delta}$  based compounds that shows alternate layers of fully oxygenated octahedral coordination and oxygen deficient tetrahedral coordination.

The structural analysis is performed firstly on the octahedral and tetrahedral volume changes. The result is depicted in Fig. 4 together with those of the other two compounds reproduced from ref [25].

One observes that the Fe-doped sample shows the more significant changes in octahedral volume with respect to that of the SYCO “mother” compound, while the tetrahedral volume remains relatively unaffected.

The result of further analysis presented in Fig. 5 shows the relative effects of in-plane and out-of-plane bond lengths between the Co cation and the neighboring O anions in the octahedral and tetrahedral coordinated structures. It is clear that only the  $\text{Co}_2\text{-O}$  bond length in the octahedral layer displays the relatively active response to the corresponding doping process. Specifically, the Fe-doped sample shows relatively larger increase of the apical bond lengths  $l_{\text{Co}_2\text{-O}_2}$  of about  $0.05\text{\AA}$  compared to those of the other compounds. This is consistent with the larger volume change of the sample shown earlier.

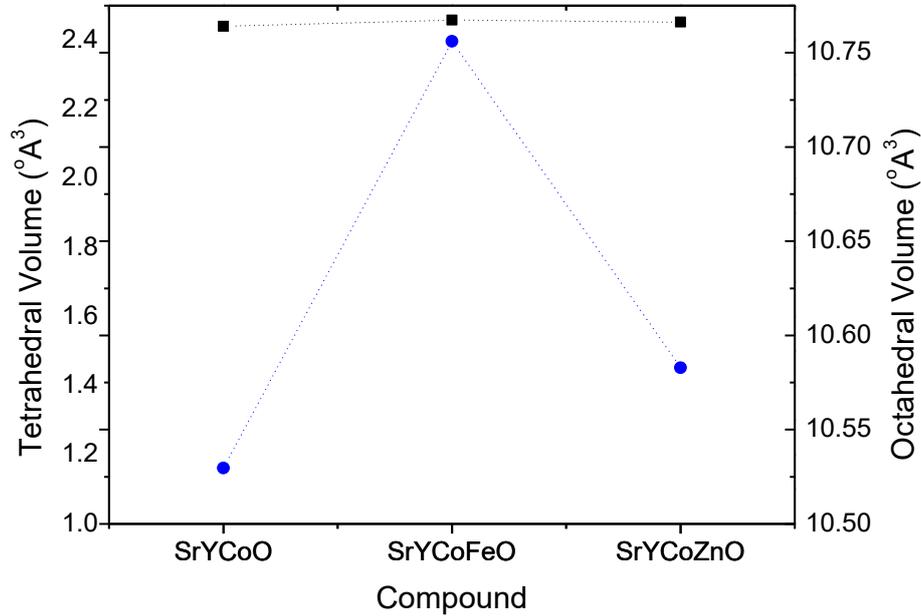


Fig. 4. Volume variations of tetrahedral (black square) and octahedral (blue circle) layer of the three compounds deduced from the refinement results of the associated XRD data.

Meanwhile, the in-plane bond length of  $l_{\text{Co2-O1}}$  is relatively unaffected by the different dopants, which varies within the miniscule range of 1.915–1.917 Å. We shall henceforth focus on the local structural changes in the octahedral layer since the most pronounced difference in the extra dopant induced magnetic behavior is exhibited on the  $M-H$  curves.

An additional analysis is performed to deduce the in-plane bond angles in the basal planes of the octahedral coordination, defined by  $\alpha = \angle(\text{Co2-O1-Co2})$ . The results are presented in Fig. 6 for the same compounds considered in Fig. 4. These bond angles are related with the distances between a certain Co ion and its adjacent neighbor of another Co ion or Fe dopant ion. A larger (smaller)  $\alpha$  implies a longer (shorter) separation between the two neighboring ions. The size of each angle may therefore serve as an indication of the magnetic interaction between the magnetic ions in the associated layers.

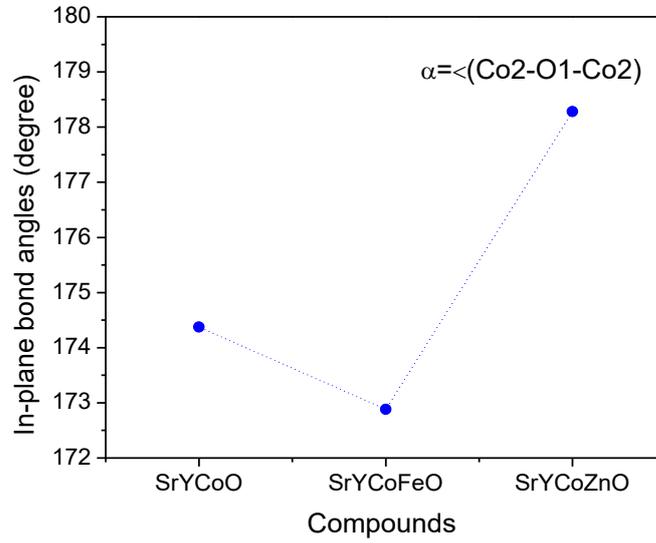


Fig. 5 Variations of in-plane (■) and out-of-plane (□) bond lengths in tetrahedral (Co1-O) as well as in-plane (●), out-of-plane (○) bond lengths in octahedral (Co2-O) coordinations. Note that O4 denotes the unoccupied oxygen site in the tetrahedral layer.

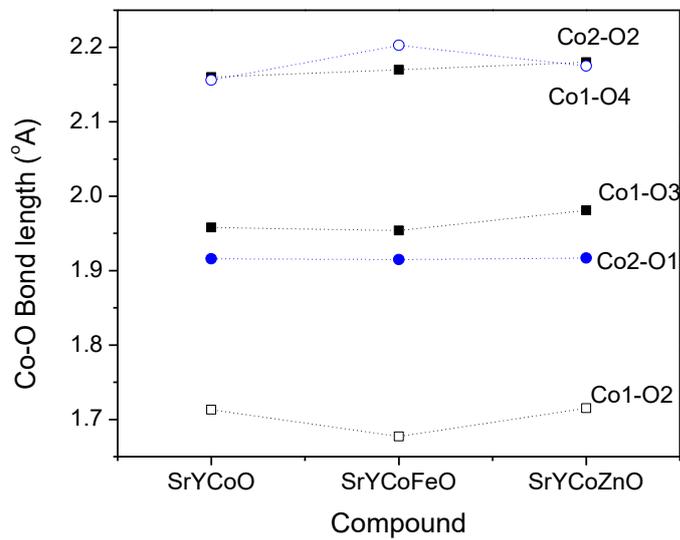


Fig. 6. Variations of the bond angle  $\alpha = \angle(\text{Co2-O1-Co2})$  in the equatorial planes of octahedral coordination, which are deduced from the refinement results of XRD data.

The local structure data given in Figs. 4, 5 and 6 further entails the following physical implications. The relatively large apical distance  $l_{\text{Co2-O2}}$  in the Fe doped sample shown by Fig. 5 is supposed to decrease the crystal field induced energy splitting  $\Delta_{\text{CF}}$  on the Co ions. In turn, it is expected to raise the Co<sup>3+</sup> spin state from the IS to HS in the octahedral layer. Further, Fig. 6 shows that the same sample has the slightly smaller  $\alpha$  and hence more effective in-plane AFM interaction in the octahedral layer thereby reducing the spin imbalance and the related ferrimagnetic component. Consequently, this may, following Ref. [21], lead to the observed suppression of FM signal in the Fe-doped compound as evidenced in Fig. 1(d). In the Zn-doped compound, on the other hand, the in-plane (Co2-O1) and apical (Co2-O2) bond lengths in the octahedral layer are both relatively unchanged with respect to those of SYCO compound. This suggests the presence of similar alternate IS and HS states of the Co<sup>3+</sup> ions in the octahedral layers that makes it possible to retain roughly the same small FM signal as revealed by the “mother” compound. Taken together, the results of local structural analysis described above have provided the plausible semi quantitative explanation of the different magnetic responses of the Fe-doped and Zn-doped compounds considered.

#### 4. Conclusion

We have shown in this report that 10% substitution of Co by non-magnetic Zn in Sr<sub>0.775</sub>Y<sub>0.225</sub>CoO<sub>3- $\delta$</sub>  retains measurable hysteretic signal instead of the total FM suppression found in the sample with the same amount of magnetic Fe doping. This study shows that the different magnetic responses are related with different dopant induced changes of the in-plane and out-of-plane (apical) Co-O bond lengths and Co-O-Co bond angle in the octahedral layers in those two compounds. It is argued that the different local structures lead to different Co<sup>3+</sup> spin states and magnetic interactions between the adjacent magnetic ions in the octahedral layers. The two combined effects suggest the effective spin cancellation in the Fe-doped sample while the Zn-doped sample is shown to retain more or less the same local structure as the SYCO mother compound and correspondingly similar hysteretic signal.

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