Cationic distribution, exchange interactions, and relaxation dynamics in Zn-diluted MnCo₂O₄ nanostructures

Tiwari, Nidhi; Pramanik, P.; Joshi, D. C.; Sarkar, T.; Pittala, S.; Salman, O. O.; Manga, M.-M.; Thota, S.

2019

Pramanik, P., Joshi, D. C., Tiwari, N., Sarkar, T., Pittala, S., Salman, O. O., . . . Thota, S. (2019). Cationic distribution, exchange interactions, and relaxation dynamics in Zn-diluted MnCo₂O₄ nanostructures. *Journal of Applied Physics*, 125(12), 124302-.
doi:10.1063/1.5079800

<https://hdl.handle.net/10356/86246>

<https://doi.org/10.1063/1.5079800>

© 2019 The Author(s). All rights reserved. This paper was published by AIP in *Journal of Applied Physics* and is made available with permission of The Author(s).

Downloaded on 26 Apr 2023 22:10:40 SGT

Cationic distribution, exchange interactions, and relaxation dynamics in Zn-diluted MnCo_2O_4 nanostructures

Cite as: J. Appl. Phys. 125, 124302 (2019); doi: 10.1063/1.5079800

Submitted: 3 November 2018 · Accepted: 9 March 2019 ·

Published Online: 27 March 2019

P. Pramanik,¹ , D. C. Joshi,¹ , N. Tiwari,² T. Sarkar,³ , S. Pittala,⁴ , O. O. Salman,⁵ M.-M. Manga,⁵ and S. Thota^{1,a)}

AFFILIATIONS

¹Department of Physics, Indian Institute of Technology, Guwahati 781039, Assam, India

²Energy Research Institute, Nanyang Technological University, Singapore

³Department of Engineering Sciences, Solid State Physics, Box 534, Uppsala University, Uppsala 75121, Sweden

⁴Department of Physics, Indian Institute of Science, Bangalore 560012, Karnataka, India

⁵Institute for Complex Materials, IFW Dresden, Helmholtzstraße 20, D-01069 Dresden, Germany

^{a)}Author to whom correspondence should be addressed: subhasht@iitg.ac.in

ABSTRACT

We report an experimental investigation of the electronic structure and magnetic properties of bulk and nanosized MnCo_2O_4 diluted with Zn. The cationic distribution for tetrahedral A-site dilution is $(\text{Co}^{2+}_{1-y_A}\text{Zn}^{2+}_{y_A})_A[\text{Mn}^{3+}\text{Co}^{3+}]_B\text{O}_{4\pm\delta}$, whereas B-site dilution results in $(\text{Co}^{2+})_A[\text{Mn}^{3+}_{1-x_B}\text{Zn}^{2+}_{x_B}\text{Co}^{3+}]_B\text{O}_{4-\delta}$. The strength of exchange interaction J_{ij} between the magnetic ions in a bulk spinel lattice decreases by $\sim 15\%$ for A-site dilution relative to the undiluted compound; however, B-site dilution results in an enhancement in J_{ij} by 17%. The frequency and temperature dependence of dynamic-susceptibility $[\chi_{ac}(f, T)]$ studies of nanostructured compounds reveals the existence of spin-glass like behavior below the freezing temperature $T_F \sim 125.7$ K (for $x_B = 0.2$) and 154.3 K ($y_A = 0.1$). Relaxation time τ follows the Power-Law variation with a dynamical critical exponent $z\nu = 6.17$ and microscopic spin relaxation time $\tau_0 = 4.4 \times 10^{-15}$ s for $x_B = 0.2$ (for $y_A = 0.1$, $z\nu = 5.2$ and $\tau_0 = 5.4 \times 10^{-13}$ s). The amplitude and peak position in $\chi_{ac}(T)$ decreases with an increase in the DC bias field, which indicates that the spin-glass phase can survive in the presence of low fields forming a critical line with an exponent 2/3. This behavior is similar to the de Almeida-Thouless (AT-line) analysis in the T-H phase diagram which supports the existence of spin-glass like behavior below T_F in these Zn diluted spinels.

Published under license by AIP Publishing. <https://doi.org/10.1063/1.5079800>

I. INTRODUCTION

Oxides with spinel crystal structure (AB_2O_4) are recognized as the holy grail for many technological applications as well as from a fundamental point of view. Such oxides with binary and ternary cations found a wide range of applications in the renewable/sustainable energy sector such as in fuel cells, batteries, and catalysis.^{1–6} Among a variety of spinel compounds, the binary transition metal oxides like MnCo_2O_4 , ZnCo_2O_4 , and their composites have gained enormous popularity as compared to other compounds because of their unique characteristics useful for electrochemical energy storage and magneto-electronics.^{7–9} These inverse-spinel systems are stable for supercapacitor applications because they can be synthesized under numerous morphologies at reduced dimensions,

such as core-shell nanoflowers, nanocages, nanorods, nanowall arrays, and porous urchin-like hierarchical architectures.^{6,8,10,11} Recently, Zhao *et al.* demonstrated that the core-shell nanowire arrays of Co_3O_4 – MnCo_2O_4 exhibit remarkable electrochemical performance with a high specific capacitance (736.5 F g^{-1}) at a current density of 1 mA cm^{-2} , which is almost twice that of the pristine compound Co_3O_4 (370.67 F g^{-1}).¹² Wu *et al.* reported that the hollow nanotubes of Ni-doped MnCo_2O_4 are the suitable candidates for the anode material in sodium ion batteries which exhibit remarkable capacity retention (81% at 1 A g^{-1}) and pseudo-capacitive characteristics with ultralong life time (above 11 000 cycles).¹³ Kang *et al.* reported that dual-phase spinel MnCo_2O_4 with nitrogen-doped reduced graphene oxide can be used as a

potential hybrid Na-air battery system simultaneously with superior oxygen evolution reaction catalytic performance over the commercial Pt/C electrocatalytic system.¹⁴ Szymczewska *et al.* reported drastic variations in the microstructure and electrical properties of Fe and Cu substituted MnCo_2O_4 thin films.¹⁵ Previous experimental studies reveal weak tetragonal distortion in undoped MnCo_2O_4 bulk and thin films.^{16,17} However, such distortion is expected to relax when surface and finite size effects play a dominant role in MnCo_2O_4 .¹⁷ First principles studies based on spin-polarized GGA + U calculations performed by Li *et al.* reported that the bulk MnCo_2O_4 shows insulating behavior with a very small gap of about 0.03 eV.¹⁸ Also, the tetrahedrally coordinated Mn and Co atoms at (001) and (110) surfaces exhibit bulk like characteristics, whereas the electronic structure of octahedral Co atoms changes substantially from the bulk state into the surface state at the (001) surface of MnCo_2O_4 .¹⁸ Besides, MnCo_2O_4 exhibits ferrimagnetic properties with ordering temperature $T_C \sim 183$ K for the bulk system^{17,19} and reduced T_C ($= 130$ K) values for nanometer sized particles ($d \sim 8$ nm).¹⁷ It has been shown in the literature that the T_C values may vary markedly depending upon the oxygen stoichiometry δ as well as in $\text{MnCo}_2\text{O}_{4\pm\delta}$.²⁰ Recent studies reveal that MnCo_2O_4 nanoparticles exhibit memory and aging effects, spin-glass like characteristics below the freezing point $T_F = 144.8$ K (with $\tau_F = 6.01$ and $\tau_0 \sim 6.18 \times 10^{-15}$ s) together with a finite size scaling of T_C ($T_C(d) = T_C(\infty)[1 - (\xi_0/d)^\lambda]$, $\lambda = 0.75 \pm 0.15$, and $\xi_0 = 1.4 \pm 0.3$ nm).^{17,19,21} Moreover, a significant reduction of T_C (167 K) was noticed with the incorporation of Jahn-Teller active ion Cu at the octahedral Co(B) sites of MnCo_2O_4 .¹⁹ On the other hand, Bhowmik and Ranganathan reported that the substitution of 50 at. % of Ru at the Mn site leads to a further decrease of T_C (100 K) together with the signatures of pinning effects in domain wall dynamics.²² On the basis of temperature dependence of ac and dc-resistivity [$\rho(T)$] measurements, these authors also reported the existence of short-range interactions in the paramagnetic regime ($T > T_C$), which leads to the formation of small polarons.²² Ruthenium incorporation in MnCo_2O_4 leads to some interesting results in $\rho(T)$ including the colossal magnetoresistance properties with a semiconductor to metallic transition below 80 K. These authors also reported a simple scaling law analysis in $\text{Mn}_{0.5}\text{Ru}_{0.5}\text{Co}_2\text{O}_4$ to classify the short-range magnetic interactions which are difficult to probe using conventional magnetization experiments.²² These studies motivated us to investigate the role of a nonmagnetic Zn substitution (both at the octahedral B and at the tetrahedral A sites) on the physical and chemical properties of MnCo_2O_4 that has not yet been explored and is the subject of this article.

The purpose of this work is to investigate the effects of Zn-dilution on the global magnetic ordering under reduced dimensions and probe the changes occurring in the electronic and crystal structures of the spinel lattice of MnCo_2O_4 . Our experimental observations reveal that bulk grain size samples of MnCo_2O_4 with Zn dilution at both tetrahedral A(y_A) and octahedral B(x_B) sites lead to reduced T_N values as compared to the undiluted compound with significant alteration in the magnetic moments and exchange interaction between the magnetic ions, whereas the nanostructures of $\text{Mn}_{0.8}\text{Zn}_{0.2}\text{Co}_2\text{O}_4$ and $\text{MnCo}_{1.9}\text{Zn}_{0.1}\text{O}_4$ exhibit spin-glass behavior below the freezing temperatures 125.7 K and 154.3 K, respectively.

II. EXPERIMENTAL DETAILS

Polycrystallites of Zn-doped MnCo_2O_4 samples with bulk and nanometer size grains were synthesized by the standard solid-state-reaction method and the sol-gel process, respectively. For the sol-gel process, alcoholic solutions of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{ZnC}_4\text{H}_6\text{O}_4 \cdot 2\text{H}_2\text{O}$, and oxalic acid were mixed together in a Pyrex beaker with 2:1 molar ratio of metals to oxalic acid. The dropwise addition of oxalic acid leads to the formation of a pink color thick gel which was dried between 80 °C and 120 °C to obtain a pink color powder. This oven dried product was calcined in air at 700 °C for 4 h to obtain the desired compounds $\text{Mn}_{1-x_B}\text{Zn}_{x_B}\text{Co}_2\text{O}_4$ and $\text{MnCo}_{2-y_A}\text{Zn}_{y_A}\text{O}_4$, whereas these compounds with bulk grain size samples were synthesized by the solid state reaction method using the precursors cobalt(II,III) oxide, manganese(IV) oxide, and zinc oxide. Stoichiometric amounts of these materials were mixed in an agate mortar and sintered in air at 1100 °C for 8 h to obtain bulk grain size samples. For the optimization of the calcination temperature and to study the formation mechanism of the compounds ($\text{Mn}_{1-x_B}\text{Zn}_{x_B}\text{Co}_2\text{O}_4$ and $\text{MnCo}_{2-y_A}\text{Zn}_{y_A}\text{O}_4$) from the oven-dried mixed oxalate product, we used a thermogravimetric analyzer (NETZSCH STA 449F3). Such a thermal study (not shown here) has been performed by measuring the weight loss of the sample from 30 °C to 1000 °C with a scan rate of 10 K/min under an Argon gas ambient with a flow rate of 60 ml/min. These studies reveal that any temperature above 500 °C yields the desired spinel compound. For the elemental analysis of the samples, a dual source X-ray photoelectron spectroscope (with Al- K_α at 1486.8 eV and Mg- K_α at 1253.6 eV) from VG Microtech equipped with an ultra-high vacuum (8×10^{-10} Torr) chamber with a pass energy of 100 eV was employed. The XPS spectra were recorded using monochromatized Al- K_α radiation. The structural characterization was performed by the high-resolution Rigaku X-ray diffractometer (of Cu- K_α radiation with $\lambda = 1.54$ Å) followed by the Rietveld refinement (FullProf program). For the microstructure analysis, we used the transmission electron microscope (TEM, JEOL JEM Model: 2100) operating at 200 keV under the secondary-electron (SE) mode. All the low-temperature magnetization measurements, including the frequency dependence of ac-magnetic susceptibility, were performed using a SQUID based magnetometer MPMS from Quantum Design.

III. RESULTS AND DISCUSSIONS

A. Electronic structure using X-ray photoelectron spectroscopy

In order to understand the electronic structure of investigated compounds, we have performed X-ray photoelectron spectroscopy (XPS). Figure 1 shows the high-resolution narrow-scan XPS spectra of Zn substituted MnCo_2O_4 samples at two different sites, i.e., at the octahedral “Mn” site ($x_B = 0.2$) and at the tetrahedral “Co” site ($y_A = 0.1$), respectively. The core-level photoelectron intensity of (i) Zn-2p, (ii) Mn-2p, (iii) Co-2p, and (iv) O-1s was plotted as a function of binding energy (eV). The binding energy of the carbon C-1s orbital (~ 284.8 eV) was used for the calibration of all these core-level spectra. For $x_B = 0.2$, the Zn-2p core level spectrum is

FIG. 1. X-ray photoelectron spectra (XPS) of 2p and 1s levels of Zn, Mn, Co, and O present in $\text{Mn}_{1-x_B}\text{Zn}_{x_B}\text{Co}_2\text{O}_4$ ($x_B = 0.2$) and $\text{MnCo}_{2-y_A}\text{Zn}_{y_A}\text{O}_4$ ($y_A = 0.1$) compounds. Figures (i), (ii), (iii), and (iv) correspond to the core level XPS spectra of Zn-2p, Mn-2p, Co-2p, and O-1s for the composition $x_B = 0.2$, whereas figures (v), (vi), (vii), and (viii) represent the core level spectra of the atoms Zn-2p, Mn-2p, Co-2p, and O-1s for $y_A = 0.1$.

deconvoluted into two highly sharp and symmetrical peaks located at 1021.09 eV and 1044.17 eV, as shown in Fig. 1(i). This doublet is associated with Zn-2p_{3/2} and Zn-2p_{1/2} core levels.^{23–26} The binding energy separation between these two peaks, often characterized as the spin-orbit splitting $\Delta \sim 23.08$ eV, confirms the divalent oxidation state of Zn in the $\text{Mn}_{0.8}\text{Zn}_{0.2}\text{Co}_2\text{O}_4$ matrix.^{23,26} Similar results were observed for the “Zn” in $\text{MnCo}_{1.9}\text{Zn}_{0.1}\text{O}_4$, where a slight shift in the binding energies of the Zn-doublet towards higher binding energies [Fig. 1(v)] was observed with $\Delta \sim 23.14$ eV, which confirms the thin Zn²⁺ state in the A-site diluted sample.

The photoelectron spectrum of the “Mn” ion in $x_B = 0.2$ and $y_A = 0.1$ sample from the 2p core-level is shown in Figs. 1(ii) and 1(vi), respectively. For $x_B = 0.2$, the spectrum is resolved into three peaks, two main peaks at 642.62 eV and 654.23 eV, and one broad satellite peak at 662.18 eV. On the other hand, for $y_A = 0.1$, the Mn-2p core level spectrum is deconvoluted into two major peaks centred at 642.17 eV and 653.61 eV without any signature of the broad satellite peak. For the deconvolution procedure, we have applied a fitting constraint on the full width at half maximum (FWHM) of the peak profile (FWHM should range within 0.2 eV). The binding energy separation between the “Mn” doublet ($\Delta \sim 11.61$ eV and 11.44 eV for $x_B = 0.2$ and $y_A = 0.1$, respectively)

signifies the trivalent oxidation state of “Mn” (i.e., Mn³⁺) inside the polycrystalline samples.^{19,26,27} The observed value of spin orbit splitting in these systems is slightly higher (~ 0.40 eV and ~ 0.23 eV for $x_B = 0.2$ and $y_A = 0.1$) as compared to the undiluted MnCo_2O_4 (~ 11.21 eV).¹⁹ This could be associated with the screening of “Mn³⁺” ions by additional “Zn” ions present in the $x_B = 0.2$ and $y_A = 0.1$ matrix.²⁸ Such additional splitting could also be due to enhanced Jahn-Teller distortion and crystal-field effects due to Zn substitution.²⁹

The core-level XPS spectra of Co-2p deconvoluted into four major peaks identified as doublets of Co(II) and Co(III), with four broad satellite peaks for both the composition $x_B = 0.2$ and $y_A = 0.1$, are shown in Figs. 1(iii) and 1(vii), respectively. The spin-orbit splitting (ΔE) between the doublet $\Delta E_{\text{Co}^{3+}}(2p_{1/2} - 2p_{3/2})$ and $\Delta E_{\text{Co}^{2+}}(2p_{1/2} - 2p_{3/2})$, which comes out to be 15.36 eV (15.21 eV) and 15.78 eV (15.59 eV), respectively, signifies the two different oxidation states of Co, i.e., Co³⁺ and Co²⁺, in both systems, $\text{Mn}_{0.8}\text{Zn}_{0.2}\text{Co}_2\text{O}_4$ and $\text{MnCo}_{1.9}\text{Zn}_{0.1}\text{O}_4$.^{19,27} Finally, the O-1s spectrum for $x_B = 0.2$ [Fig. 1(iv)] is deconvoluted into two Gaussian-Lorentzian (GL) peaks centered at 530.15 eV and 531.73 eV.^{27,30} The origin of the most intense peak at 530.15 eV is associated with the bonding between metal and lattice oxygen, i.e.,

TABLE I. The list of parameters obtained from the temperature dependent inverse magnetic susceptibility data $\chi^{-1}(T)$ of undoped MnCo_2O_4 , $\text{Mn}_{1-x_B}\text{Zn}_{x_B}\text{Co}_2\text{O}_4$, and $\text{MnCo}_{2-y_A}\text{Zn}_{y_A}\text{O}_4$ Bulk (B) and nano-particles (NPs) using the Néel's expression for ferrimagnets. The oxygen stoichiometries are $\delta_1 \sim 0.13$, $\delta_2 \sim 1.7$, $\delta_3 \sim 1.82$, and $\delta_4 \sim 0.3$. Total magnetic moment of system = μ_{Total} ; asymptotic Curie temperature = T_a ; molecular field constant = (λ_{ij}) ; and exchange constants = E_{ij} .

Sample name	μ_{Total}	$\mu(\text{A})$ [$\mu(\text{B})$]	(T_a)	λ_{ij}	J_{ij}/k_B
$(\text{Co}_{0.85}\text{Zn}_{0.09})_A[\text{Mn}_{0.9}\text{Co}_{0.9}]_B\text{O}_{4-\delta_1}$ (NP)	$7.88 \mu_B$	$3.3 \mu_B$ [$7.1 \mu_B$]	652.9 K	$\lambda_{AA} = 21.11^a$ $\lambda_{BB} = 72.12$ $\lambda_{AB} = 117.8$	$J_{AA} = 3.96$ $J_{BB} = 18.06$ $J_{AB} = 14.74$
$(\text{Co}_{0.86}\text{Zn}_{0.08})_A[\text{Mn}_{0.99}\text{Co}_{0.88}]_B\text{O}_{4+\delta_2}$ (B)	$7.98 \mu_B$	$3.32 \mu_B$ [$7.25 \mu_B$]	507.5 K	$\lambda_{AA} = 3.46^a$ $\lambda_{BB} = 51.5$ $\lambda_{AB} = 98.8$	$J_{AA} = 0.65$ $J_{BB} = 12.88$ $J_{AB} = 12.36$
$(\text{Co}_{1.11})_A[\text{Mn}_{0.77}\text{Zn}_{0.2}\text{Co}]_B\text{O}_{4-\delta_3}$ (NP)	$7.5 \mu_B$	$4.3 \mu_B$ [$6.2 \mu_B$]	681.1 K	$\lambda_{AA} = 27.1^a$ $\lambda_{BB} = 103.2$ $\lambda_{AB} = 107.5$	$J_{AA} = 5.1$ $J_{BB} = 25.8$ $J_{AB} = 13.45$
$(\text{Co}_{0.9})_A[\text{Mn}_{0.8}\text{Zn}_{0.2}\text{Co}_{0.9}]_B\text{O}_{4-\delta_4}$ (B)	$7.74 \mu_B$	$3.83 \mu_B$ [$6.73 \mu_B$]	527.9 K	$\lambda_{AA} = 46.57^a$ $\lambda_{BB} = 53.15$ $\lambda_{AB} = 100.6$	$J_{AA} = 8.74$ $J_{BB} = 13.3$ $J_{AB} = 12.59$
$(\text{Co})_A[\text{MnCo}]_B\text{O}_4$ (NP)	$7.92 \mu_B$	$3.87 \mu_B$ [$7.03 \mu_B$]	717.6 K	$\lambda_{AA} = 43.8^{17}$ $\lambda_{BB} = 85.2$ $\lambda_{AB} = 110.9$	$J_{AA} = 8.18$ $J_{BB} = 21.3$ $J_{AB} = 13.8$
$(\text{Co})_A[\text{MnCo}]_B\text{O}_4$ (B)	$8.1 \mu_B$	$3.87 \mu_B$ [$7.11 \mu_B$]	496.8 K	$\lambda_{AA} = 41.5^{17}$ $\lambda_{BB} = 36.8$ $\lambda_{AB} = 87.1$	$J_{AA} = 7.7$ $J_{BB} = 9.24$ $J_{AB} = 10.9$

^aUsing occupancy number of individual atoms from Rietveld refinement.

Mn–O, Zn–O, and Co–O,³⁰ while the low intense peak at 531.73 eV is associated with the surface-adsorbed oxygen.^{27,30} However, the oxygen spectra (O-1s) shown in Fig. 1(viii) for the $y_A = 0.1$ system has been resolved into three GL peaks centered at 529.9 eV, 530.79 eV, and 533.4 eV associated with the oxygen-metal bonding, surface oxygen, and some additional oxygen at surface, respectively.²⁷ Thus, on the basis of the analysis gathered from the Rietveld refinement analysis of the XRD data and electronic states obtained from XPS results, we determined the following cationic distribution: $(\text{Co}^{2+}_{1-y_A}\text{Zn}^{2+}_{y_A})_A[\text{Mn}^{3+}\text{Co}^{3+}]_B\text{O}_{4\pm\delta}$ and $(\text{Co}^{2+})_A[\text{Mn}^{3+}_{1-x_B}\text{Zn}^{2+}_{x_B}\text{Co}^{3+}]_B\text{O}_{4-\delta}$ for $y_A = 0.1$ and $x_B = 0.2$, respectively. Table I summarizes a detailed cationic distribution with oxygen stoichiometry (δ) for the bulk and nanostructures separately for both A- and B-site dilutions in comparison with the undoped MnCo_2O_4 .

B. Crystal structure and morphology

The room temperature XRD analysis reveals the formation of the spinel cubic phase with the $Fd-3m$ space group for both the compositions $\text{Mn}_{1-x_B}\text{Zn}_{x_B}\text{Co}_2\text{O}_4$ ($x_B = 0.2$) and $\text{MnCo}_{2-y_A}\text{Zn}_{y_A}\text{O}_4$ ($y_A = 0.1$) under bulk and nanostructures. For bulk grain size systems, the lattice parameter $a_0 = 8.266 \text{ \AA}$ and $8.283 \text{ \AA}$, for the compositions $x_B = 0.2$ and $y_A = 0.1$, respectively. Whereas, for the nanoparticles of size 60 nm and 31 nm, we obtained $a_0 = 8.233 \text{ \AA}$ (for $x_B = 0.2$) and $8.270 \text{ \AA}$ (for $y_A = 0.1$). A detailed comparison of these diffraction patterns is shown in the supplementary material (Fig. S1). Thus, the size reduction leads to a decrease in the unit cell volume, as has been seen previously in other oxides.^{31,32} In the

case of bulk samples above a critical composition x_c (0.2) and y_c (0.1), ZnO emerges as a secondary phase; therefore, we have chosen the two compositions $\text{Mn}_{0.8}\text{Zn}_{0.2}\text{Co}_2\text{O}_4$ and $\text{MnCo}_{1.9}\text{Zn}_{0.1}\text{O}_4$ as optimistic compounds to study the detailed magnetic and electronic properties. Magnitudes of crystallite size d , estimated from the Williamson-Hall analysis of the X-ray line broadening, are consistent with the average particle size obtained from the histogram analysis of size distribution of particles observed from the transmission electron microscope. Figures 2(a) and 2(b) show the bright-field TEM images of $\text{MnCo}_{1.9}\text{Zn}_{0.1}\text{O}_4$ and $\text{Mn}_{0.8}\text{Zn}_{0.2}\text{Co}_2\text{O}_4$ nano-powders obtained after calcination in air at 700°C for 4 h. Both these micrographs clearly show the formation of spherical particles with an average size of $\sim 31 \text{ nm}$ and 60 nm , respectively, obtained from the histogram analysis fitted with log-normal distribution. The corresponding selected area electron diffraction (SAED) pattern is shown in the insets (c) and (d), signifying the crystalline nature of the sample. Figures 2(e) and 2(f) show the high-resolution-transmission electron microscope (HRTEM) image which gives the uniform lattice spacing of $2.5 \text{ \AA}$ and $2.48 \text{ \AA}$ consistent with the interplanar spacing d_{hkl} corresponding to the Miller indices (311) of lattice planes, which is the highest intensity diffraction peak obtained in the x-ray diffraction pattern for the nanocrystallite of compositions $x_B = 0.2$ and $y_A = 0.1$.

C. Magnetic properties

In this section, we discuss the magnetic properties of bulk and nanocrystallites of A- and B-site diluted MnCo_2O_4 . Figure 3 shows

FIG. 2. The transmission-electron micrographs (TEMs) (a) of $\text{MnCo}_{1.9}\text{Zn}_{0.1}\text{O}_4$ and (b) $\text{Mn}_{0.8}\text{Zn}_{0.2}\text{Co}_2\text{O}_4$ nanocrystallites. The corresponding selected area electron diffraction patterns are shown in (c) and (d). Figures (e) and (f) show the high resolution TEM images for $y_A = 0.1$ and $x_B = 0.2$, respectively. Figures (g) and (h) show the histogram analysis for $y_A = 0.1$, $x_B = 0.2$ nanocrystalline fitted with log-normal size distribution.

the temperature dependence of low-field (50 Oe) DC-magnetic susceptibility ($\chi = M/H_{DC}$) of (i) $\text{MnCo}_{1.9}\text{Zn}_{0.1}\text{O}_4$ and (ii) $\text{Mn}_{0.8}\text{Zn}_{0.2}\text{Co}_2\text{O}_4$ nanoparticles measured under zero-field-cooled (ZFC) and field-cooled (FC) conditions. The insets of Fig. 3 show $\chi_{ZFC}(T)$ measured in the presence of various DC-fields between $H_{DC} = 50$ Oe and 30 kOe. A giant bifurcation was noticed between χ_{ZFC} and χ_{FC} ($\Delta\chi = \chi_{FC} - \chi_{ZFC} \sim 0.145 \text{ emu g}^{-1} \text{ Oe}^{-1}$ and $0.058 \text{ emu g}^{-1} \text{ Oe}^{-1}$) below the peak temperatures of $\chi_{ZFC}(T)$ at 125.3 K and 155.2 K for $x_B = 0.2$ and $y_A = 0.1$, respectively, signifying the superparamagnetic (SPM) blocking/or spin-glass (SG) freezing behavior of these nanoparticles, whereas the magnitude of χ_{FC} gradually decreases and approaches a minimum value at 127 K for $x_B = 0.2$ and 157 K for $y_A = 0.1$, respectively. Figure 4 shows the comparison of the field-cooled susceptibility curves $\chi_{FC}(T)$ of nanocrystallites with the bulk grain size samples. Clearly, for the nanocrystallites, the magnitude of $\chi_{FC}(T)$ and ordering temperatures are smaller as compared to their bulk counterpart as well as the undoped MnCo_2O_4 case. For the compositions $x_B = 0.2$ and $y_A = 0.1$, the ordering temperatures are 127 K and 157 K, respectively which are still smaller than the nanocrystallites of the undoped MnCo_2O_4 case (165 K).²¹ As seen from the inset of Fig. 3, the peak in χ_{ZFC} significantly shifts towards lower temperatures with increasing H_{DC} typical to SPM or SG behavior [$T_p \sim 125.3$ K (for 50 Oe) and 15.4 K (for 10 kOe) for $x_B = 0.2$]. Similarly, a shift was noticed in the case of $y_A = 0.1$, $T_p \sim 155.2$ K (for 50 Oe) and 15.2 K (for 10 kOe).

In order to distinguish the SPM or SG state in these nanoparticle systems, we have performed the temperature dependence of ac-magnetic susceptibility $\chi_{ac}(T)$ across the transition for different frequencies (f) between 0.17 Hz and 1202 Hz and at different bias fields H_{DC} . Therefore, below we focus our discussion mainly on the $\chi_{ac}(T, f)$ and a detailed analysis of $\chi_{ac}(T, H_{DC})$.

Figures 5(a) and 5(b) show the temperature variation of real-component [$\chi'(T)$ shown on the left-hand-side scale] and imaginary component [$\chi''(T)$ shown on the right-hand-side scale] of the $\chi_{ac}(T)$ for different values of f ($0.17 \text{ Hz} \leq f \leq 1202 \text{ Hz}$) for both the nanocrystalline compounds $x_B = 0.2$ and $y_A = 0.1$. One can clearly notice a cusp in both $\chi'(T)$ and $\chi''(T)$ with a clear shift of the maximum point of the cusp towards the high temperature side with increasing f . Such a frequency dispersion of the cusp maximum signifies the glassy nature of the system. In order to confirm such a dynamic response of $\chi_{ac}(T)$, we used the conventional model of spin dynamics “critical slowing down in spin-glasses” (Power-law scaling of the relaxation time: $\tau = \tau_0[(T/T_F) - 1]^{-z\nu}$).³³ In the above expression, the parameter τ_0 represents the relaxation time constant, T_F is the spin-glass freezing temperature, z is the dynamic critical exponent, and ν is the critical exponent of the correlation length. Figure 5(c) shows the variation of $\ln \tau$ vs $\ln[(T/T_F) - 1]$, where straight lines represent least-square-fit of the experimental data performed using the Power-law described above. Linear variation of $\ln \tau$ and best-fitting to the experimental data suggest that the spin-glass behavior of nanoparticles and the mathematical fitting leads to the following parameters: $\tau_0 = 4.4 \times 10^{-15} \text{ s}$, $T_F = 125.7 \text{ K}$, and $z\nu = 6.17$ for $x_B = 0.2$ using the frequency variation of $\chi'(T)$. However, for the $y_A = 0.1$ system, τ_0 turns out to be $5.4 \times 10^{-13} \text{ s}$, $T_F = 154.3 \text{ K}$, and $z\nu = 5.2$. Large magnitudes of τ_0 observed in these nanoparticle systems confirm the presence of interacting magnetic nanoparticles similar to the NiO nanorods coated with oleic acid ($3.2 \times 10^{-14} \text{ s}$), Ni dispersed in silica ($1.22 \times 10^{-11} \text{ s}$), $\text{La}_{0.91}\text{Sr}_{0.09}\text{CoO}_3$ ($3 \times 10^{-15} \text{ s}$), $\text{CaBaFe}_4\text{O}_{7+0.14}$ ($7.3 \times 10^{-10} \text{ s}$), and Fe_3O_4 nanoparticles.^{34–38} Usually standard spin-glass system shows the relaxation time constant “ τ_0 ” values between 10^{-9} and 10^{-16} s and the critical exponent values between 4 and 12.³³ Furthermore, the relative shift ($\Omega = \Delta T_f/[T_f(\Delta f)]$) of the peak temperature per

FIG. 3. Temperature dependence of DC-magnetic susceptibility (χ) measured under both ZFC and FC conditions under $H_{DC} = 50$ Oe for Zn-doped MnCo_2O_4 [(i) $y_A = 0.1$ and (ii) $x_B = 0.2$] nanocrystals. Insets of these figures show χ_{ZFC} measured at different DC fields [(a) 50 Oe, (b) 500 Oe, (c) 1000 Oe, (d) 5000 Oe, (e) 1 T, and (f) 3 T].

decade frequency for both the systems lies within the range of spin-glass systems (0.0045–0.06).

However, to estimate the activation energy of spins in the glassy state, we used another scaling law known as the Vogel-Fulcher law, $\tau = \tau_0 \exp[E_a/k_B(T_f - T_0)]$.³⁹ Here, T_0 is a measure of the interparticle interaction strength on magnetic relaxation, τ_0 represents the relaxation time constant, k_B is the Boltzmann constant, and E_a is the activation energy. A wide literature study related to the frequency dependent ac-magnetic susceptibility data claims that Power-law provides better legitimacy for the existence of a spin-glass state.⁴⁰ Therefore, using τ_0 values obtained from the Power-law analysis, we plotted the $1/\ln(\tau/\tau_0)$ vs T_f graph [Fig. 5(d)] and fitted the experimental data to the Vogel-Fulcher law which yields the following fitting parameters: $\tau_0 = 4.4 \times 10^{-15}$ s, and $E_a = 81.3 k_B$, and $T_0 = 123.8$ K for $x_B = 0.2$ nanocrystalline sample ($\tau_0 = 5.4 \times 10^{-13}$ s, $E_a = 60.5 k_B$, $T_0 = 152.7$ K for $y_A = 0.1$). Previous studies by Souletie and Tholence reported the

FIG. 4. Field cooled susceptibility (χ_{FC}) vs temperature (T) plots of bulk and nanocrystalline $\text{MnCo}_{2-y_A}\text{Zn}_{y_A}\text{O}_4$ and $\text{Mn}_{1-x_B}\text{Zn}_{x_B}\text{Co}_2\text{O}_4$ for the compositions $y_A = 0.1$ and $x_B = 0.2$, respectively.

relationship between the Vogel-Fulcher law and the Power-law as $\ln\left(\frac{40k_B T_0}{E_a}\right) \sim \frac{25}{z\nu}$.⁴⁰ Using this relation, we have calculated the magnitude of $z\nu = 5.4$ (for $y_A = 0.1$ nps) and 6.08 (for $x_B = 0.2$ nps), which are close to 5.2 (for $y_A = 0.1$) and 6.17 (for $x_B = 0.2$) obtained from the Power-law analysis. The effective anisotropy constant K_{eff} estimated using the expression $E_a = 25k_B T_P (=K_{\text{eff}}V)$ turns out to be $\sim 3.4 \times 10^4$ erg/cm³ and 3.7×10^3 erg/cm³ for $x_B = 0.2$ and $y_A = 0.1$, respectively, whereas the magnitude of surface anisotropy constant K_S calculated using the expression $K_S S = 25k_B T_P$ for the nanoparticles of compositions $y_A = 0.1$ and $x_B = 0.2$ is 0.4×10^{-2} erg/cm² and 1.7×10^{-2} erg/cm², respectively. These values are consistent with the previously reported data for similar types of spinel compounds. For example, $K_{\text{eff}} = 3.7 \times 10^5$ erg/cm³ and 6.3×10^5 erg/cm³ for the nanocrystallites of $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ (size ~ 80 nm) and Fe_3O_4 (size ~ 8.4 nm), respectively.^{41,42}

Figure 6 shows $\chi_{ac}(T)$ for both the samples $x_B = 0.2$ and $y_A = 0.1$, measured at a constant $f (= 51$ Hz) and $h_{ac} = 3$ Oe of ac-field superimposed with different DC-bias fields (H_{DC}) between 10 Oe and 300 Oe. Clearly, the magnitude of χ' and χ'' decreases significantly with a gradual shift in their peak position towards lower temperatures with increasing H_{DC} , which is a typical characteristic of the glassy system. Such magnetic behavior with increasing H_{DC} can be described by the de Almeida-Thouless (AT) line criterion $[T_P(H) \propto T_{P_0} \left(1 - \frac{H}{H_c}\right)^{\frac{2}{3}}]$.^{38,43} Here, AT line defines the onset of a transition from the frozen spin-glass like state to the reversible magnetic behavior at the peak temperature T_{P_0} in ac-susceptibility under the zero bias-field. The insets shown in Figs. 6(a) and 6(c) represent the variation of peak maximum temperature (T_P) of χ' plotted as a function of $H^{2/3}$. Hollow symbols in the inset of Fig. 6 represent the experimentally obtained $T_P(H)$ values for different magnitudes of H_{DC} , and the straight line is the best-fit for the AT-line equation. Extrapolation of the AT-line

FIG. 5. Temperature variation of the real (left-hand-side scale) and imaginary components (right-hand-side scale) of the ac-magnetic susceptibility $\chi_{ac}(T)$ for (a) $x_B = 0.2$ and (b) $y_A = 0.1$ nanocrystallites recorded at various frequencies (f) for $H_{DC} = 0$ Oe using the ac-magnetic field amplitude $h_{ac} = 4$ Oe. Figures (c) and (d) show the $\ln \tau$ vs $\ln[(T/T_F) - 1]$ and $1/\ln(\tau/\tau_0)$ vs T_F corresponding to the Power law and the Vogel-Fulcher law, respectively. The solid circular and square symbols represent the peak temperature obtained from χ' for the compositions $x_B = 0.2$ and $y_A = 0.1$, respectively, and the solid lines are least square fits to the experimental data.

back to zero H_{DC} provides the spin-glass freezing temperature $T_F \sim 156.4$ K and 127.7 K for the compositions $y_A = 0.1$ and $x_B = 0.2$, respectively. It is possible that T_P cannot be accurately represented because of the variation in nanoparticle size distribution, which causes a large change in the interparticle interactions and average freezing temperatures. The competition between the magnetic dipolar interactions and the aligning magnetic field leads to a spin-glass like behavior in these nanocrystallites. Besides, the $H^{2/3}$ dependence of T_P also suggests the diverging relaxation times due to the competing interactions among the disordered surface-spins than the spins residing in the core of nanoparticles. Usually, the AT-line analysis along with the Power-law is used as one of the tests to identify the spin-glass properties in various magnetic systems, including the nanostructures and bulk compounds.^{40,44–46}

Lower magnetic ordering temperatures (142.05 K $\rightarrow$ 127 K, for $x_B = 0.2$) and reduced magnetization values (9.315 emu/g $\rightarrow$ 4.997 emu/g, for $x_B = 0.2$) in the nanostructured samples as compared to the bulk signify the dominant role of surface and finite size effects on the global magnetic ordering of these Zn diluted $MnCo_2O_4$ systems. As a consequence of the randomly oriented spins structure with a low co-ordination number at the vicinity of the surface of the nanostructures, we expect that the spin-glass behavior emerged. Moreover, the absence of any noticeable frequency dispersion in $\chi_{ac}(T, f)$ of the bulk samples as compared to the nanoparticles further supports the inference that the magnetic behavior of these site diluted $MnCo_2O_4$ nanostructures is strongly dependent on the size of the crystallites. It is a well-known fact that a significant rise in the surface-to-volume ratio of the nanoparticles results in an increase in the missing bonds of the surface atoms and a number of defects (oxygen vacancies). Such issues have significant implications in the magnetic ordering of the currently investigated system; for example, Bazuev and Korolyov reported that nonstoichiometric $MnCo_2O_4$ ($MnCo_2O_{4+\delta}$) exhibits reduced ordering temperatures 67.5 K and 167.5 K for $\delta \sim 0.62$ and 0.275, respectively.²⁰ In the present case also, Zn diluted $MnCo_2O_4$ nanoparticles show a lower-crystallinity as compared to the bulk samples because of the low heat treatment conditions ($\leq 700^\circ\text{C}$), which finally results in cation-deficiency and excess oxygen content. In the present case, Zn has been simultaneously substituted in the system during the solution stage of the synthesis. On the basis of the thermogravimetric and differential scanning calorimetry analysis, together with the crystal structure analysis, we found that B-site diluted nanostructured samples exhibit a higher oxygen deficiency as compared to the A-site diluted compound. Such nonstoichiometry may play a major role in deciding the magnetic characteristics along with the finite-size effects of the nanostructured samples.

Generally, the substitution of the nonmagnetic elements inside the spinel matrix leads to the altered exchange interactions and disorderness inside the system. Such site disorder and competing magnetic interactions between the cations usually cause destruction of the long-range order and lead to a disordered magnetic state. Such a disordered magnetic configuration at low-temperatures is often called “reentrant spin-glass behavior.”^{47,48} The magnetic frustration in the current investigated system may be arising from such disordered ground-state spin configurations.^{49–55} Generally, two

FIG. 6. Temperature dependence of the real (χ') and imaginary (χ'') component of ac-magnetic susceptibility (χ_{ac}) for different bias fields H_{DC} ($0 \text{ Oe} \leq H_{DC} \leq 300 \text{ Oe}$) of Zn diluted MnCo_2O_4 nanocrystallites at the A-site for the composition $y_A = 0.1$ [(a) and (b)] and Zn diluted at the B-site with the composition $x_B = 0.2$ [(c) and (d)] recorded. These measurements are performed at a constant frequency $f = 51 \text{ Hz}$ and an ac-field amplitude $h_{ac} = 4 \text{ Oe}$. The inset shows the variation of peak temperature (T_P) plotted as a function of $H_{DC}^{2/3}$ for both the compositions. Here, the solid lines represent least-squares fitting of the experimental data with de Almeida-Thouless equation.

closely spaced transitions can be noticed in the temperature dependence of differential susceptibility curves, in which the high temperature transition is associated with the longitudinal spin component that vanishes across the T_N and the second transition occurs just below the T_N at which the transverse spin component freezes-in. In the present case, for the diluted bulk system, the ground-state spin configuration is likely to be canted locally (non-vanishing ferrimagnetic bulk magnetization) without any signatures of glassy characteristics, whereas the nanoparticles after Zn dilution exhibit a spin-glass-like behavior as evident from $\chi_{ac}(T, f)$ data. It is well known that no long-range magnetic order takes place if the magnetic ions are so diluted that there is no percolation boundary, and a spin-glass-like behavior is usually observed around the percolation threshold, 20 at. %_{at-B-site} and 10 at. %_{at-A-site} of Zn in MnCo_2O_4 . The electric charge fluctuations that result from the large charge difference between the cations are possibly marked off by lattice distortions. Such random distortions may yield random anisotropy effects mainly on the B sites, thereby leading to frustrated state. Needless to say that, the topology of the B sublattice (pyrochlore lattice) is particularly favorable to the development of geometrical frustration in many spinels.⁵⁶

Figure 7 shows the temperature dependence of inverse paramagnetic susceptibility [$\chi_{ZFC}^{-1}(T)$] of both bulk and nanocrystallites above 145 K. Here, the circles in different colors represent the experimental data points recorded under the ZFC condition, and the solid color line represents the fits to the Néel's expression for ferrimagnets given by $(1/\chi) = (T/C) + (1/\chi_0) - [\sigma_0/(T-\theta)]$.⁵⁷ The list of fitting parameters for both these compositions, including the case of undoped MnCo_2O_4 , is given in Table I.

For bulk grain sized samples, we obtained the following parameters: $\chi_0 = 0.0157 \text{ emu/mol Oe}$ (0.0142), $\sigma_0 = 584.7 \text{ mol Oe K/emu}$

(712.7), $C = 7.98 \text{ emu K/mol Oe}$ (7.5), $\theta = 162.7 \text{ K}$ (140.8) for $y_A = 0.1$ and $x_B = 0.2$. On the other hand, we obtained the following parameters: $\chi_0 = 0.012 \text{ emu/mol Oe}$ (0.0103), $\sigma_0 = 481.04 \text{ mol Oe K/emu}$ (846.3), $C = 7.78 \text{ emu K/mol Oe}$ (7.05), and $\theta = 160.0 \text{ K}$ (131.6) for the nanocrystallites of $y_A = 0.1$ and $x_B = 0.2$. The difference in the magnitudes of these fitting

FIG. 7. Temperature dependence of inverse magnetic susceptibility [$\chi^{-1}(T)$] of Zn diluted MnCo_2O_4 nanocrystallites and bulk grain size compounds of [(i) nano and (iii) bulk] $\text{Mn}_{1-x_B}\text{Zn}_{x_B}\text{Co}_2\text{O}_4$ for $x_B = 0.2$, [(ii) nano and (iv) bulk] $\text{MnCo}_{2-y_A}\text{Zn}_{y_A}\text{O}_4$ for $y_A = 0.1$. The solid line represents the best fitting of Néel's expression for the ferrimagnets.

parameters mainly results from the surface effects and dissimilar temperature dependence of the magnetic moments located at the tetrahedral A and the octahedral B sites. By means of the following relation of Curie-constant $C = N\mu_{\text{eff}}^2/3k_B$, we have estimated the effective magnetic moment $\mu_{\text{eff}} = 7.88\mu_B$ and $7.5\mu_B$ per formula units (f.u.) for the nanocrystallites of $y_A = 0.1$ and $x_B = 0.2$, respectively. These magnitudes are significantly lower than their bulk counterparts ($8\mu_B$ and $7.74\mu_B$ for $y_A = 0.1$ and $x_B = 0.2$, respectively).

Nevertheless, these magnitudes are smaller as compared to the undoped MnCo_2O_4 case $\mu_{\text{eff}} = 7.92\mu_B$ ($8.1\mu_B$) for nano (bulk) systems. As compared to the bulk crystals, the magnitude of magnetic moments is slightly lower in the case of nanoparticles due to the finite size and surface effects.⁵⁸ On the other hand, the asymptotic Curie temperature, T_a , is usually defined as the ratio of C and the fitting parameter χ_0 which is generally represented as the strength of the antiferromagnetic exchange coupling between the spins located at the tetrahedral A and octahedral B sites of the spinel lattice. In the present case, we obtained $T_a = 652.9\text{ K}$ and 681.1 K for the nanocrystallites of $y_A = 0.1$ and $x_B = 0.2$, respectively.

For the bulk grain sized sample, the magnitude of T_a turns out to be 507.5 K and 527.9 K for the Zn substitution at the tetrahedral(A)-Co site and the octahedral(B)-Mn site of MnCo_2O_4 . Moreover, we have evaluated the molecular field constants [$\lambda_{AA} \sim 21.11$ (27.1), $\lambda_{BB} \sim 72.2$ (103.2), and $\lambda_{AB} \sim 117.8$ (107.5)] and antiferromagnetic exchange constant [$J_{AA}/k_B \sim 3.9\text{ K}$ (5.1 K), $J_{BB}/k_B \sim 18.06\text{ K}$ (25.8 K), and $J_{AB}/k_B \sim 14.7\text{ K}$ (13.4 K)] for $\text{MnCo}_{1.9}\text{Zn}_{0.1}\text{O}_4$ and $\text{Mn}_{0.8}\text{Zn}_{0.2}\text{Co}_2\text{O}_4$ nanoparticles, respectively. These constants follow the general trends $\lambda_{AB} > |\lambda_{BB}|$, $|\lambda_{AA}|$ for spinels and these constant values are all positive for most systems.⁵⁷ The substitution of Zn at the Mn and Co sites significantly alters the strength of exchange interaction between the magnetic ions in the spinel MnCo_2O_4 as compared to the undiluted case [$J_{AA}/k_B \sim 7.75\text{ K}$ (8.2 K), $J_{BB}/k_B \sim 9.2\text{ K}$ (21.3 K), and $J_{AB}/k_B \sim 10.9\text{ K}$ (13.8 K)] for bulk (nanostructure) (Table I). Furthermore, when Zn is diluted at the tetrahedral A-site, the exchange interaction between the magnetic ions significantly decreases by $\sim 15\%$ (for the case of nanoparticles) as compared to the undiluted case (39% of bulk samples). Nevertheless, B site dilution leads to an increase in the exchange interaction by 17% (for nano) and a decrease by 37.5% (for the bulk grain size compounds). Such interaction has significant implications in the global magnetic ordering of the system, for example, the effective magnetic moment μ_{eff} obtained from $\chi^{-1}(T)$ is $\sim 7.5\mu_B$ for 20 at. % Zn dilution with B-site contribution $6.2\mu_B$ arising from Mn^{3+} and Co^{3+} , which is slightly lower than $\mu_{\text{eff}} = 7.88\mu_B$ for 10 at. % of Zn dilution at tetrahedral A sites.

Usually, the incorporation of the non-magnetic element within the magnetically ordered system interrupts the exchange interactions between magnetic ions (J_{AB} , J_{BB} , and J_{AA}). Generally, all these three interactions are of antiferromagnetic in nature and they are of comparable strength, except some for some special cases, where J_{BB} dominates over the other two, which may lead to the development of geometrical frustration. In the present case, the highest Zn dilution 20 at. % (x_B) was achieved at the octahedral B-sites, which is still below the percolation threshold ($x_{\text{Th}} \sim 33\%$) of trivalent manganese and divalent cobalt ions for a significant alteration of the long range magnetic ordering. On the other hand,

FIG. 8. The magnetization vs field (M-H) hysteresis curves of (a) $\text{Mn}_{1-x_B}\text{Zn}_{x_B}\text{Co}_2\text{O}_4$ ($x_B = 0.2$) and (b) $\text{MnCo}_{2-y_A}\text{Zn}_{y_A}\text{O}_4$ ($y_A = 0.1$) nanoparticles measured at temperature $T = 5\text{ K}$ under both ZFC and FC.

only 10 at. % (y_A) of Zn dilution was attained in the case of the tetrahedral A-sites, which is also less than the standard x_{Th} . Our analysis reveals that the overall strength in all these three exchange interactions drops to $\sim 3.2\%$ when the B-site Zn dilution increases 10 at. % more than the A-site dilution for the bulk samples. However, in the case of the nanostructured samples, this difference is much higher ($\sim 30\%$), due to which the magnetic ordering of these samples are showing significantly different magnetic properties with glassy characteristics as compared to their bulk counterparts. Nonetheless, in both the dilutions, J_{BB} is still significantly higher than J_{AA} and comparable in strength with J_{AB} . It is well known that no long-range magnetic order exists if the magnetic ions are heavily diluted and a disordered state like a spin-glass-like behavior arises near the B-site percolation threshold ($x_{\text{Th}} \sim 0.4$).^{59,60} For example, spinel oxides like TiFe_2O_4 , TiCo_2O_4 , and SnCo_2O_4 undoubtedly display spin-glass characteristics, except the composition $\text{Ti}_{0.3}\text{Mg}_{1.3}\text{Fe}_{1.44}\text{O}_4$, in which the trivalent Fe composition reaches 45%.^{61–67} These important findings are further supported by the magnetization vs field (M-H) hysteresis loops measured at $T = 5\text{ K}$ for both the nanocrystallite samples of composition $x_B = 0.2$ and $y_A = 0.1$ (Fig. 8). These M-H loops yield the saturation magnetization $M_S = 14.11\text{ emu/g}$ for $y_A = 0.1$ and $M_S = 8.98\text{ emu/g}$ for $x_B = 0.2$. The coercive field $H_C = 4516\text{ Oe}$ for $x_B = 0.2$ is greater than the $H_C = 3963\text{ Oe}$ for $y_A = 0.1$. Also, no significant exchange bias was observed when the compound was cooled down to 5 K under the 20 kOe DC-field.

IV. CONCLUSIONS

On the basis of a detailed crystal structure analysis, two different compositions are chosen for a maximum level of Zn dilution at the octahedral-B and tetrahedral-A sites of the inverse spinel MnCo_2O_4 ($\text{Mn}_{1-x_B}\text{Zn}_{x_B}\text{Co}_2\text{O}_4$, $x_B = 0.2$ and $\text{MnCo}_{2-y_A}\text{Zn}_{y_A}\text{O}_4$, $y_A = 0.1$). The electronic structure obtained from the analysis of x-ray photoelectron spectra and Rietveld

refinement of x-ray diffraction data reveals the following cationic distribution: $(\text{Co}_{1-y_A}^{2+}\text{Zn}_{y_A}^{2+})_A[\text{Mn}^{3+}\text{Co}^{3+}]_B\text{O}_{4\pm\delta}$ and $(\text{Co}^{2+})_A[\text{Mn}_{1-x_B}^{3+}\text{Zn}_{x_B}^{2+}\text{Co}^{3+}]_B\text{O}_{4-\delta}$. A systematic study of the dc and ac-magnetic susceptibility of the above compounds under a reduced dimension shows that they exhibit spin-glass like characteristics with freezing temperatures $T_F \sim 125.7\text{ K}$ ($x_B = 0.2$) and $T_F \sim 154.3\text{ K}$ ($y_A = 0.1$). However, the bulk samples exhibit ferrimagnetic ordering with Néel temperature $T_N \sim 142.05\text{ K}$ ($x_B = 0.2$) and 164.8 K ($y_A = 0.1$). The antiferromagnetic exchange constants (J_{ij}) evaluated from the temperature dependence of inverse paramagnetic susceptibility $\chi^{-1}(T)$ and using Néel's expression for ferrimagnets show the general trend $J_{AB} > J_{BB} > J_{AA}$ for both the spinels. As compared to the undiluted case, the A-site dilution leads to a decrease in the overall exchange interaction between the magnetic ions by $\sim 15\%$ for nanoparticles and $\sim 39\%$ in the case of bulk samples. Nevertheless, B site dilution leads to an increase in the exchange interaction by 17% (for nano) and a decrease by 37.5% (for bulk). The effective magnetic moment μ_{eff} obtained from $\chi^{-1}(T)$ is $\sim 7.5\mu_B$ for $x_B = 0.2$ with B-site contribution $6.2\mu_B$ arising from trivalent Mn and Co, which is slightly lower than the $\mu_{\text{eff}} = 7.88\mu_B$ for $y_A = 0.1$.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for a comparative representation of the X-ray diffraction pattern together with Rietveld refinement data for (a) $\text{Mn}_{1-x_B}\text{Zn}_{x_B}\text{Co}_2\text{O}_4$ ($x_B = 0.2$, nanoparticles), (b) $\text{MnCo}_{1-y_A}\text{Zn}_{y_A}\text{O}_4$ ($y_A = 0.1$ nanoparticles), (c) $x_B = 0.2$ (bulk grain size compound), and (d) $y_A = 0.1$ (bulk grain size compound) calcined at 700°C and sintered at 1100°C for 4 h in air. The red color symbols represent the experimental data, and black color solid lines are the theoretically simulated patterns. The blue lines shown at the bottom represent the difference between the intensities of the observed (I_{obs}) and the simulated (I_{theory}) patterns. The olive color vertical line represents the Bragg positions.

ACKNOWLEDGMENTS

P.P. acknowledges the FIST programme of the Department of Science and Technology, India, for partial support of this work (Ref. No. SR/FST/PSII-020/2009 and SR/FST/PSII-037/2016). P.P. and D.C.J. acknowledge the central instrument facility (CIF) of the Indian Institute of Technology Guwahati for partial support of this work. T.S. acknowledges support from the VR starting grant (No. 2017-05030).

REFERENCES

- G. Huang, S. Xu, Z. Xu, H. Sun, and L. Li, *ACS Appl. Mater. Interfaces* **6**, 21325 (2014).
- J. Li, J. Wang, X. Liang, Z. Zhang, H. Liu, Y. Qian, and S. Xiong, *ACS Appl. Mater. Interfaces* **6**, 24 (2013).
- X. Cao, J. Wu, C. Jin, J. Tian, P. Strasser, and R. Yang, *ACS Catal.* **5**, 4890 (2015).
- S. Thota and S. Singh, in *Magnetic Spinel—Synthesis, Properties and Applications*, edited by M. S. Seehra (IntechOpen, Rijeka, 2017), Chap. 4.
- T. Nissinen, T. Valo, M. Gasik, J. Rantanen, and M. Lampinen, *J. Power Sources* **106**, 109 (2002).
- X. Wu, W. Wu, K. Wang, W. Chen, and D. He, *Mater. Lett.* **147**, 85 (2015).
- L. Li, Y. Zhang, X. Liu, S. Shi, X. Zhao, H. Zhang, X. Ge, G. Cai, C. Gu, X. Wang *et al.*, *Electrochim. Acta* **116**, 467 (2014).
- Y. Dong, Y. Wang, Y. Xu, C. Chen, Y. Wang, L. Jiao, and H. Yuan, *Electrochim. Acta* **225**, 39 (2017).
- B. Liu, B. Liu, Q. Wang, X. Wang, Q. Xiang, D. Chen, and G. Shen, *ACS Appl. Mater. Interfaces* **5**, 10011 (2013).
- Y. Zhao, L. Hu, S. Zhao, and L. Wu, *Adv. Funct. Mater.* **26**, 4085 (2016).
- W. Li, K. Xu, G. Song, X. Zhou, R. Zou, J. Yang, Z. Chen, and J. Hu, *CrystEngComm* **16**, 2335 (2014).
- L. Zhao, M. Yang, Z. Zhang, Y. Ji, Y. Teng, Y. Feng, and X. Liu, *Inorg. Chem. Commun.* **89**, 22 (2018).
- L. Wu, J. Lang, P. Zhang, X. Zhang, R. Guo, and X. Yan, *J. Mater. Chem. A* **4**, 18392 (2016).
- Y. Kang, D. Zou, J. Zhang, F. Liang, K. Hayashi, H. Wang, D. Xue, K. Chen, K. R. Adair, and X. Sun, *Electrochim. Acta* **244**, 222 (2017).
- D. Szymczewska, S. Molin, P. V. Hendriksen, and P. Jasiński, *Crystals* **7**, 185 (2017).
- K. J. Kim and J. W. Heo, *J. Korean Phys. Soc.* **60**, 1376 (2012).
- S. Singh, P. Pramanik, S. Sangaraju, A. Mallick, L. Giebler, and S. Thota, *J. Appl. Phys.* **121**, 194303 (2017).
- Y. Li, M. Wu, and C. Ouyang, *Appl. Surf. Sci.* **349**, 510 (2015).
- P. Pramanik, S. Thota, S. Singh, D. C. Joshi, B. Weise, A. Waske, and M. Seehra, *J. Phys. Condens. Matter* **29**, 425803 (2017).
- G. Bazuev and A. Korolyov, *J. Magn. Magn. Mater.* **320**, 2262 (2008).
- S. Thota, S. K. Das, A. Kumar, S. Sangaraju, and B. C. Choi, *IEEE Trans. Magn.* **49**, 1020 (2013).
- R. Bhowmik and R. Ranganathan, *Phys. Rev. B* **74**, 214417 (2006).
- X. Liu, H. Liu, W. Zhang, X. Li, N. Fang, X. Wang, and J. Wu, *Nanoscale Res. Lett.* **10**, 195 (2015).
- C. Wagner, W. Riggs, L. Davis, J. Moulder, and G. Muilenberg, in *Handbook of X-ray Photoelectron Spectroscopy* (Perkin-Elmer Corporation, Eden Prairie, MN, 1979), pp. 74–80.
- S. Ameen, M. S. Akhtar, H.-K. Seo, Y. S. Kim, and H. S. Shin, *Chem. Eng. J.* **187**, 351 (2012).
- D. Joshi, S. Nayak, P. Suresh, K. Suresh, B. M. Kumar, and S. Thota, *Phys. Status Solidi B* **252**, 2323 (2015).
- S. Wang, Y. Hou, and X. Wang, *ACS Appl. Mater. Interfaces* **7**, 4327 (2015).
- M. van Veenendaal, *Phys. Rev. B* **74**, 085118 (2006).
- L. Piper, N. Quackenbush, S. Sallis, D. Scanlon, G. Watson, K.-W. Nam, X.-Q. Yang, K. Smith, F. Omenya, N. Chernova *et al.*, *J. Phys. Chem. C* **117**, 10383 (2013).
- T.-H. Ko, K. Devarayan, M.-K. Seo, H.-Y. Kim, and B.-S. Kim, *Sci. Rep.* **6**, 20313 (2016).
- T. Sarkar, B. Ghosh, A. Raychaudhuri, and T. Chatterji, *Phys. Rev. B* **77**, 235112 (2008).
- T. Sarkar, A. Raychaudhuri, and T. Chatterji, *Appl. Phys. Lett.* **92**, 123104 (2008).
- A. Mydosh, *Spin Glasses: An Experimental Introduction* (Taylor and Francis (CRC Press), London, 1993).
- V. Singh, M. Seehra, and J. Bonevich, *J. Appl. Phys.* **105**, 07B518 (2009).
- H. Shim, A. Manivannan, M. Seehra, K. Reddy, and A. Punnoose, *J. Appl. Phys.* **99**, 08Q503 (2006).
- J. Wu and C. Leighton, *Phys. Rev. B* **67**, 174408 (2003).
- T. Sarkar, V. Duffort, V. Pralong, V. Caignaert, and B. Raveau, *Phys. Rev. B* **83**, 094409 (2011).
- M. Suzuki, I. S. Fullem, I. S. Suzuki, L. Wang, and C.-J. Zhong, *Phys. Rev. B* **79**, 024418 (2009).
- J. Tholence, *Solid State Commun.* **35**, 113 (1980).
- J. Souletie and J. Tholence, *Phys. Rev. B* **32**, 516 (1985).
- K. Parekh and R. V. Upadhyay, *J. Appl. Phys.* **107**, 053907 (2010).
- O. Moscoso-Londoño, P. Tancredi, D. Muraca, P. M. Zélis, D. Coral, M. F. van Raap, U. Wolff, V. Neu, C. Damm, C. de Oliveira *et al.*, *J. Magn. Magn. Mater.* **428**, 105 (2017).

- ⁴³F. Jiménez-Villacorta, J. Sánchez-Marcos, E. Céspedes, M. García-Hernández, and C. Prieto, *Phys. Rev. B* **82**, 134413 (2010).
- ⁴⁴J. de Almeida and D. J. Thouless, *J. Phys. A Math. Gen.* **11**, 983 (1978).
- ⁴⁵C. Lacabanne and D. Chatain, *J. Phys. Chem.* **79**, 283 (1975).
- ⁴⁶D. Thouless, J. de Almeida, and J. Kosterlitz, *J. Phys. C Solid State Phys.* **13**, 3271 (1980).
- ⁴⁷J. Srivastava, J. Kulkarni, S. Ramakrishnan, S. Singh, V. Marathe, G. Chandra, V. Darshane, and R. Vijayaraghavan, *J. Phys. C Solid State Phys.* **20**, 2139 (1987).
- ⁴⁸M. Gabay and G. Toulouse, *Phys. Rev. Lett.* **47**, 201 (1981).
- ⁴⁹J. Villain, *J. Phys. C Solid State Phys.* **10**, 1717 (1977).
- ⁵⁰J. Villain, *J. Phys. C Solid State Phys.* **11**, 745 (1978).
- ⁵¹P. Anderson, *J. Less Common Metals* **62**, 291 (1978).
- ⁵²B. Derrida, J. Maillard, J. Vannimenus, and S. Kirkpatrick, *J. Phys. Lett.* **39**, 465 (1978).
- ⁵³R. Rammal, R. Suchail, and R. Maynard, *Solid State Commun.* **32**, 487 (1979).
- ⁵⁴H. Maletta, *Z. Phys. B* **37**, 55 (1980).
- ⁵⁵H. Maletta and W. Felsch, *Phys. Rev. B* **20**, 1245 (1979).
- ⁵⁶F. Guillou, S. Thota, W. Prellier, J. Kumar, and V. Hardy, *Phys. Rev. B* **83**, 094423 (2011).
- ⁵⁷A. H. Morrish, in *The Physical Principles of Magnetism*, edited by Allan H. Morrish (Wiley-VCH, January 2001), p. 696, ISBN 0-7803-6029-X.
- ⁵⁸X. Batlle and A. I. Labarta, *J. Phys. D Appl. Phys.* **35**, R15 (2002).
- ⁵⁹J. Hubsch, G. Gavaille, and J. Bolfa, *J. Appl. Phys.* **49**, 1363 (1978).
- ⁶⁰F. Scholl and K. Binder, *Z. Phys. B Condens. Matter* **39**, 239 (1980).
- ⁶¹R. Vanleerberghe, E. De Grave, R. Vandenberghe, and G. Robbrecht, *J. Magn. Magn. Mater.* **15**, 55 (1980).
- ⁶²C. Radhakrishnamurty, S. Likhite, and R. Nagarajan, *J. Magn. Magn. Mater.* **15**, 195 (1980).
- ⁶³S. Thota and M. Seehra, *J. Appl. Phys.* **113**, 203905 (2013).
- ⁶⁴S. Thota, V. Narang, S. Nayak, S. Sambasivam, B. Choi, T. Sarkar, M. S. Andersson, R. Mathieu, and M. Seehra, *J. Phys. Condens. Matter* **27**, 166001 (2015).
- ⁶⁵J. Hubsch and G. Gavaille, *Phys. Rev. B* **26**, 3815 (1982).
- ⁶⁶L. Corliss, J. Hastings, and F. Brockman, *Phys. Rev.* **90**, 1013 (1953).
- ⁶⁷G. Sawatzky, F. Van Der Woude, and A. Morrish, *Phys. Rev.* **187**, 747 (1969).