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# Structure and magnetism of electrospun porous high-entropy $(\text{Cr}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Co}_{1/5}\text{Ni}_{1/5})_3\text{O}_4$ , $(\text{Cr}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Co}_{1/5}\text{Zn}_{1/5})_3\text{O}_4$ and $(\text{Cr}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Ni}_{1/5}\text{Zn}_{1/5})_3\text{O}_4$ spinel oxide nanofibers†

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High-entropy oxide nanofibers, based on equimolar  $(\text{Cr},\text{Mn},\text{Fe},\text{Co},\text{Ni})$ ,  $(\text{Cr},\text{Mn},\text{Fe},\text{Co},\text{Zn})$  and  $(\text{Cr},\text{Mn},\text{Fe},\text{Ni},\text{Zn})$  combinations, were prepared by electrospinning followed by calcination. The obtained hollow nanofibers exhibited a porous structure consisting of interconnected nearly strain-free  $(\text{Cr}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Co}_{1/5}\text{Ni}_{1/5})_3\text{O}_4$ ,  $(\text{Cr}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Co}_{1/5}\text{Zn}_{1/5})_3\text{O}_4$  and  $(\text{Cr}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Ni}_{1/5}\text{Zn}_{1/5})_3\text{O}_4$  single crystals with a pure  $Fd\bar{3}m$  spinel structure. Oxidation state of the cations at the nanofiber surface was assessed by X-ray photoelectron spectroscopy and cation distributions were proposed satisfying electroneutrality and optimizing octahedral stabilization. The magnetic data are consistent with a distribution of cations that satisfies the energetic preferences for octahedral vs. tetrahedral sites and is random only within the octahedral and tetrahedral sublattices. The nanofibers are ferrimagnets with relatively low critical temperature more similar to cubic chromites and manganites than to ferrites. Replacing the magnetic cations Co or Ni with non-magnetic Zn lowers the critical temperature from 374 K ( $\text{Cr},\text{Mn},\text{Fe},\text{Co},\text{Ni}$ ) to 233 and 105 K for ( $\text{Cr},\text{Mn},\text{Fe},\text{Ni},\text{Zn}$ ) and ( $\text{Cr},\text{Mn},\text{Fe},\text{Co},\text{Zn}$ ), respectively. The latter nanofibers additionally have a low temperature transition to a reentrant spin-glass-like state.

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## Introduction

High-entropy materials (HEMs) are a new class of materials consisting in multicomponent solid solutions. Multicomponents, present in near-equimolar proportions, are randomly distributed in the lattice.<sup>1,2</sup> They are attracting enormous scientific attention due to their unique structure, enhanced

properties, novel functionalities and potential for application in many different fields ranging from catalysis to energy storage and conversion.<sup>3–20</sup>

The class of HEMs encompasses materials having bonding character spanning from metallic to ionic and a variety of structures (hexagonal, cubic, rock-salt, fluorite, perovskite, spinel...), featured by high-entropy mixing at one or two cation sublattice(s).<sup>21</sup> HEMs comprise high-entropy alloys (HEAs)<sup>1,2</sup> and high-entropy ceramics (HECs),<sup>21,22</sup> in turn including sulfides,<sup>23</sup> silicides,<sup>24</sup> nitrides,<sup>25</sup> carbides,<sup>26</sup> oxides<sup>10,27–29</sup> and other compounds.<sup>30</sup>

After the synthesis of the first single-phase multicomponent rock-salt oxide *via* solid state sintering from an equimolar mixture of binary oxides in 2015,<sup>28,31</sup> many physical or chemical routes have been followed in the last years to prepare HEMs in various forms (bulk, nanoparticles, nanosheets...).<sup>22,32–38</sup> Very recently, it has been demonstrated that high entropy oxides (HEOs) in the form of nanofibers (NFs) can be successfully prepared by the electrospinning technique.<sup>39–43</sup> Zhao *et al.*<sup>39</sup> have reported the synthesis of electrospun high entropy  $(\text{La}_{1/5}\text{Sm}_{1/5}\text{Eu}_{1/5}\text{Gd}_{1/5}\text{Tm}_{1/5})_2\text{Zr}_2\text{O}_7$  NFs with excellent thermal

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stability, whereas Xing *et al.*<sup>40</sup> have produced  $(Y_{1/5}Yb_{1/5}Sm_{1/5}Eu_{1/5}Er_{1/5})_2O_3$  NFs with cubic bixbyite structure.

High entropy rock-salt  $(Mg_{1/5}Co_{1/5}Ni_{1/5}Cu_{1/5}Zn_{1/5})O$  NFs prepared *via* electrospinning have shown interesting performance as active anode materials in rechargeable lithium ion batteries.<sup>41,42</sup> Electrospinning is a simple, versatile and cost-effective technique, widely adopted for the production of porous high aspect ratio nanostructures and suitable for the manufacturing of NFs on an industrial scale due to its scalability.<sup>44–48</sup> This paper deals with the preparation and thorough characterization of electrospun porous NFs of high-entropy  $(Cr,Mn,Fe,Co,Ni)$ ,  $(Cr,Mn,Fe,Co,Zn)$  and  $(Cr,Mn,Fe,Ni,Zn)$  oxides having spinel structure. This structure comprises a slightly distorted face-centered cubic (fcc) lattice of  $O^{2-}$  anions, where cations occupy tetrahedral 8a sites and octahedral 16d sites, thus forming two cation sublattices (Fig. S1, ESI<sup>†</sup>).<sup>49</sup> High entropy spinel oxides (HESOs) have been the focus of in-depth studies.<sup>50–57</sup>

Among them,  $(Cr_{1/5}Mn_{1/5}Fe_{1/5}Co_{1/5}Ni_{1/5})_3O_4$ , the first HESO to be reported,<sup>50</sup> has received particular attention and has been evaluated for several applications, such as electrocatalysis<sup>53,54</sup> and energy storage.<sup>52,55,58</sup> The magnetic properties of HESOs have already been summarized.<sup>59,60</sup> They are governed by the oxido-mediated superexchange interactions within and between the two cation sublattices. The magnetic properties of  $(Cr_{1/5}Mn_{1/5}Fe_{1/5}Co_{1/5}Ni_{1/5})_3O_4$ , in both bulk and nanostructured form,<sup>61–65</sup> have been the subject of several studies, which have firmly established that  $(Cr_{1/5}Mn_{1/5}Fe_{1/5}Co_{1/5}Ni_{1/5})_3O_4$  is a ferrimagnet below *ca.* 400 K. The low temperature behavior has been attributed to antiferromagnetically-coupled regions rich in Cr or Mn<sup>62</sup> or locally varying inter-site exchange interactions.<sup>65</sup> Mao *et al.*<sup>61</sup> have reported the magnetization isotherms at room temperature (RT) of  $(Cr_{1/5}Mn_{1/5}Fe_{1/5}Co_{1/5}Zn_{1/5})_3O_4$  and  $(Cr_{1/5}Mn_{1/5}Fe_{1/5}Ni_{1/5}Zn_{1/5})_3O_4$  and shown that substitution of nonmagnetic Zn<sup>2+</sup> for magnetic Co<sup>2+</sup> and Ni<sup>2+</sup> decreases the saturation and remanent magnetization, and coercive field.

Here, a detailed magnetic characterization of electrospun  $(Cr_{1/5}Mn_{1/5}Fe_{1/5}Co_{1/5}Ni_{1/5})_3O_4$ ,  $(Cr_{1/5}Mn_{1/5}Fe_{1/5}Co_{1/5}Zn_{1/5})_3O_4$  and  $(Cr_{1/5}Mn_{1/5}Fe_{1/5}Ni_{1/5}Zn_{1/5})_3O_4$  NFs is presented. These HESO-NFs display a rich and diverse magnetic behavior depending on composition. The present study confirms that  $(Cr_{1/5}Mn_{1/5}Fe_{1/5}Co_{1/5}Ni_{1/5})_3O_4$  NFs have ferrimagnetic structure between 5 and  $\approx 400$  K but, at variance with previous interpretation, the structure is non-collinear, *i.e.*, the sublattice magnetizations are not parallel. We prove that both  $(Cr_{1/5}Mn_{1/5}Fe_{1/5}Co_{1/5}Zn_{1/5})_3O_4$  and  $(Cr_{1/5}Mn_{1/5}Fe_{1/5}Ni_{1/5}Zn_{1/5})_3O_4$  NFs are paramagnetic at RT and upon cooling they first assume a non-collinear ferrimagnetic structure and then a conical/spiral or canted ferrimagnetic structure with spin-glass-like character. The qualitative similarity of the Zn-containing NFs is, however, contrasted by the largely different magnetic parameters and transition temperatures. Therefore, the magnetic structure of HESO-NFs can be easily tuned by changing just a single cation. This study paves the way to the obtainment of one-dimensional nanostructures with controlled and easily tailored magnetic properties, which is of great applicative

interest as they can potentially be used as building blocks for next-generation electromagnetic devices,<sup>66</sup> in magnetic sensors, and flexible magnets.<sup>67</sup>

## Results and discussion

### Morphology of the HESO-NFs

Based on the varying cations in the transition metal (TM) combinations, the produced  $(Cr,Mn,Fe,Co,Ni)$ ,  $(Cr,Mn,Fe,-Co,Zn)$  and  $(Cr,Mn,Fe,Ni,Zn)$  HESOs were coded as CoNi, CoZn and NiZn (Fig. S2e, ESI<sup>†</sup>).

Fig. S3 (ESI<sup>†</sup>) displays the results of the scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX) analysis on the as-calcined samples. SEM micrographs demonstrate the formation of NFs for all compositions. Nonetheless, slight changes are noticed in their morphology (Fig. S3a–c, ESI<sup>†</sup>). In sample CoNi (Fig. S3a, ESI<sup>†</sup>), where bundles of NFs alongside isolated NFs are observed, the fibers look relatively uniform in diameter along their axis. On the contrary, in samples CoZn (Fig. S3b, ESI<sup>†</sup>) and NiZn (Fig. S3c, ESI<sup>†</sup>), the diameter is not uniform along the NF axis; the variation is more marked in the case of the latter sample. The center of the NF diameter distributions (Fig. S3d–f, ESI<sup>†</sup>), as measured by the image analysis software of the microscope, decreases in the order CoNi > CoZn > NiZn. EDX analysis (Fig. S3g–i, ESI<sup>†</sup>) proves the spatially uniform distribution of oxygen and TMs throughout all samples at the micro-scale.

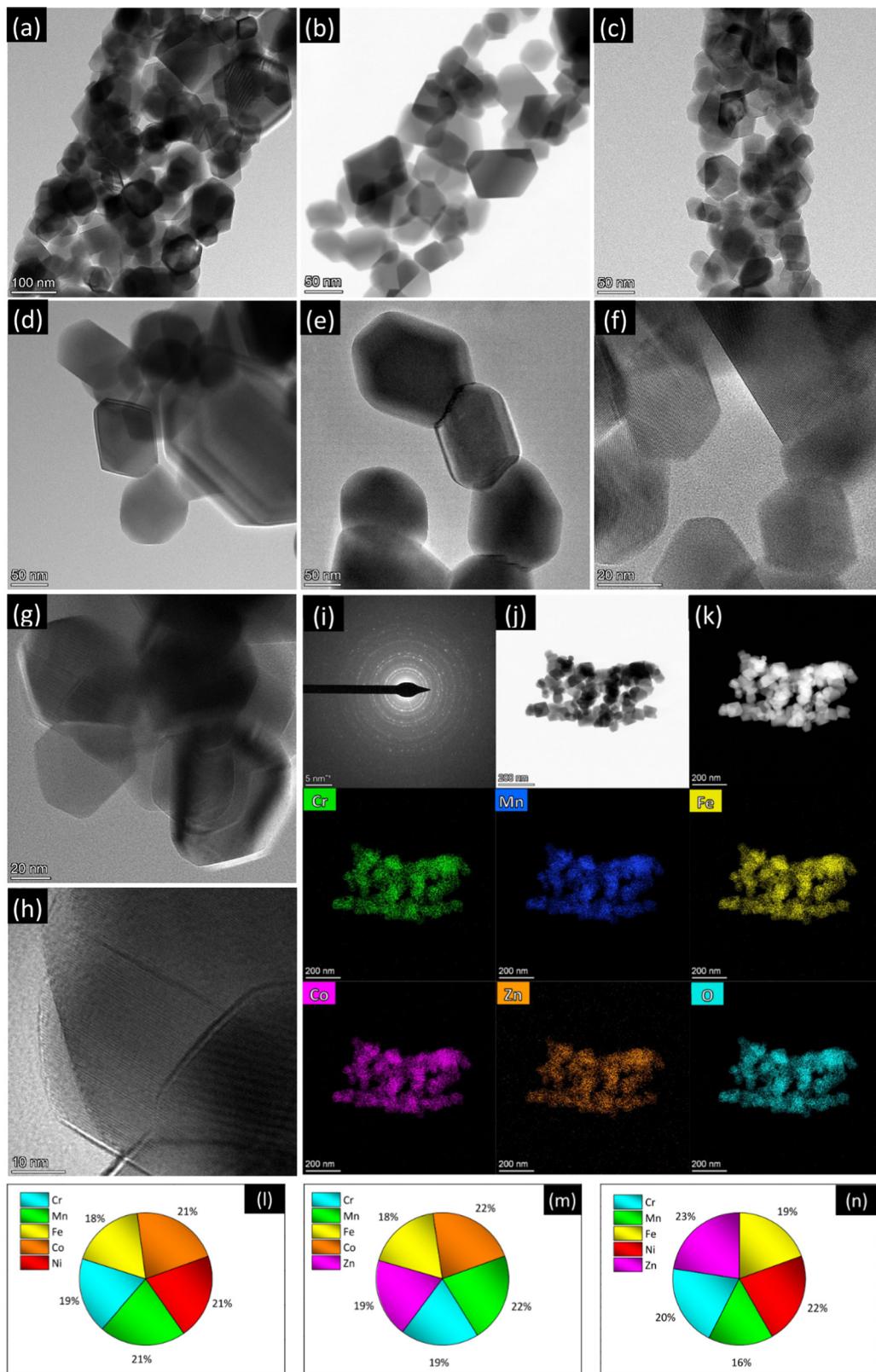
Fig. 1 and Fig. S4–S6 (ESI<sup>†</sup>) summarize the results of high-resolution transmission electron microscopy/scanning transmission electron microscopy (HRTEM/STEM)/EDX analysis. The TEM images with lower magnification (Fig. S4a, c and e, ESI<sup>†</sup>) substantially confirm the morphological picture emerged from the SEM analysis. Apart from the above-described slight differences, the morphology of the NFs exhibits common features to all the compositions. The fibers, with diameters in the 150–450 nm range, are micrometer long and featured by a coral-like structure (Fig. 1a–c), as frequently observed in electrospun oxides.<sup>68–70</sup> They consist of interconnected grains with size ranging between a few tens of nm to the hundred nm range.

Regardless of their composition, the primary oxide grains have well defined polyhedral shape, with more or less rounded vertices (Fig. 1d–h and Fig. S5, ESI<sup>†</sup>). The oxide grains are crystalline with spinel structure and randomly oriented, as proved by the diffraction rings in the selected-area electron diffraction (SAED) patterns (Fig. 1i and Fig. S6a, d, ESI<sup>†</sup>) for isolated NFs (Fig. 1j and Fig. S6b, e, ESI<sup>†</sup>). They exhibit a spinel structure. The STEM/EDX elemental maps (Fig. 1k and Fig. S6c, f, ESI<sup>†</sup>) reveal that in all samples the spatial distribution of metals and oxygen is homogeneous even at the nanometer scale.

The compositional analysis by STEM/EDX highlights the achievement of nearly equiatomic combinations of TMs (Fig. 1l–n), namely  $(Cr_{0.18}Mn_{0.21}Fe_{0.18}Co_{0.22}Ni_{0.21})$ ,  $(Cr_{0.19}Mn_{0.22}Fe_{0.18}Co_{0.22}Zn_{0.19})$  and  $(Cr_{0.20}Mn_{0.16}Fe_{0.19}Ni_{0.22}Zn_{0.23})$  for samples CoNi, CoZn and NiZn, respectively.

The homogeneity of the cation distribution is further confirmed by the projection analysis of the EDX maps (Fig. 2). The

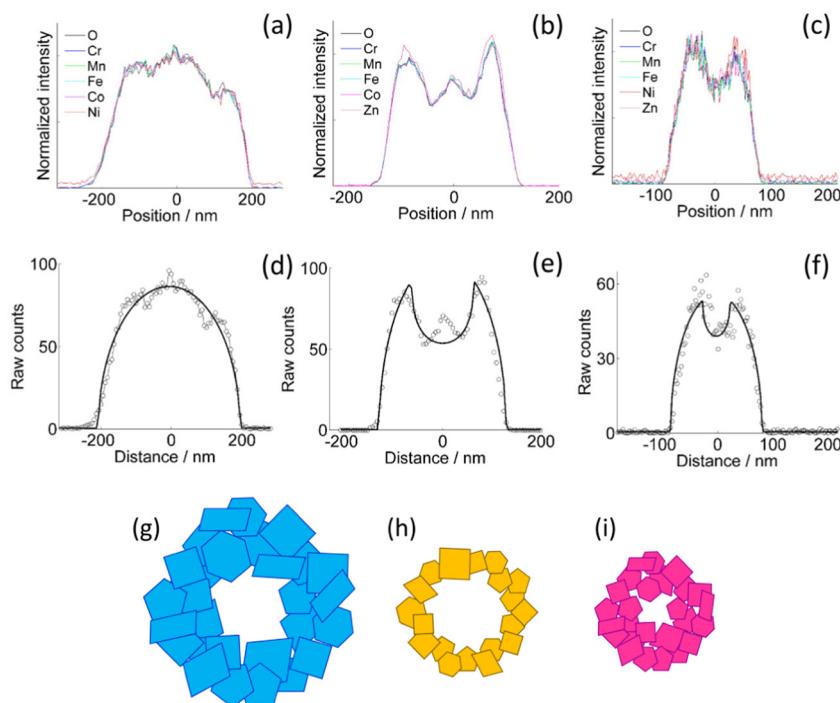




**Fig. 1** Results of the HRTEM/STEM/EDX analysis on samples (a, d, g, h and l) CoNi, (b, e, i–k and m) CoZn and (c, f and n) NiZn. (a–h) HRTEM images; (i) SAED pattern for (j) an isolated NF, (k) corresponding STEM/EDX elemental maps and (l–n) relative concentrations of the TMs.

normalized profiles of all the metals and oxygen overlap to within the experimental noise, except for a small discrepancy of

the Zn profile in the CoZn NF (Fig. 2b). Model profiles for solid or hollow NFs were fitted to the experimental oxygen profiles of



**Fig. 2** Projection analysis of the EDX elemental maps. (a–c) Projected profiles of a quasi-solid NF (a, CoNi), irregularly hollow NF (b, CoZn), and hollow NF (c, NiZn). (d–f) Experimental oxygen profiles (circles) and best-fit models (line). (g–i) Sketch of the typical cross section of (g) CoNi, (h) CoZn and (i) NiZn NFs. Note the different length scales in panels (a–f).

selected NFs (Fig. 2d–f). Comparing results for each NF, the NFs were assigned to three morphological categories, namely, quasi-solid, irregularly hollow, and hollow NF. All morphologies were observed for each NF composition and irregularly hollow NFs seem predominant in all samples. In addition to categorizing the NP morphology, the fitting procedure allowed measuring the NF outer and inner diameter of the selected NFs. The range of both diameters are collected in Table S2 (ESI<sup>†</sup>) along with that of the calculated shell thickness, and cross-section sketches of the three NF types are shown in Fig. 2g–i.

The decreasing trend of the outer NF diameter CoNi > CoZn > NiZn resulting from projection analysis agrees with the NP diameter distribution from the analysis of SEM images. Electron diffraction patterns proved that the NF comprise primary particles with spinel structure. HRTEM images of samples CoNi, CoZn and NiZn display crystal lattice fringes in primary particles that are suitably oriented with respect to the electron beam. Geometrical phase analysis (GPA) of the crystal lattice fringes allowed monitoring the crystallinity of the primary particles and the crystallographic relationship with neighboring particles (Fig. 3). Fringes were observed for the {111}, {220}, and {311} planes. No difference among the three NF samples was found, so the following discussion applies to all NF types. All fringe-displaying particles are single crystals and are free from significant strain, except for thin strained layers where the particles are in contact (Fig. 3g).

A single case in a CoNi NF was observed, where a 40 × 60 nm polyhedral, round-edged particle displays compressive strain along its free edges (Fig. 3g). It is interesting that in all cases no

significant strain is observed in the particle interior. In general, equal orientation of neighboring particles is not observed by HRTEM, even when they are face-sharing. Only in a few cases, equi-oriented particles are detected (Fig. 3b, e and h). In conclusion, GPA of HRTEM fringes showed that (i) the characteristics of the primary particles are common to the three NF samples, (ii) the primary particles are single crystals, and (iii) neighboring particles usually have different lattice orientation, the opposite is rarely detected in HRTEM images.

### Crystalline phase of the oxide

Fig. 4 shows the XRD patterns of the electrospun HESO-NFs. In all samples, the diffraction peaks correspond to the reflections of fcc spinel structure, belonging to  $Fd\bar{3}m$  space group (JCPDS no. 22-1084)<sup>51,52,56,61,71–76</sup> No additional peaks attributable to secondary phases are detected, indicating that a single-phase is formed for any composition, namely  $(Cr_{1/5}Mn_{1/5}Fe_{1/5}Co_{1/5}Ni_{1/5})_3O_4$ ,  $(Cr_{1/5}Mn_{1/5}Fe_{1/5}Co_{1/5}Zn_{1/5})_3O_4$ ,  $(Cr_{1/5}Mn_{1/5}Fe_{1/5}Co_{1/5}Ni_{1/5})_3O_4$ ,  $(Cr_{1/5}Mn_{1/5}Fe_{1/5}Co_{1/5}Zn_{1/5})_3O_4$  and  $(Cr_{1/5}Mn_{1/5}Fe_{1/5}Ni_{1/5}Zn_{1/5})_3O_4$  for samples CoNi, CoZn and NiZn, respectively. This finding is in agreement with the outcomes provided by the SAED patterns. The average size of HESO crystallites (*i.e.*, coherence length) is calculated from the full width at half maximum (FWHM) of the (331) peak, through the Scherrer's equation,  $d = k\lambda/\beta \cos \theta$ , where  $k$  (0.9) is the shape factor,  $\lambda$  is the wavelength of X-ray radiation,  $\beta$  is the FWHM in radians and  $\theta$  is the Bragg's angle.<sup>77</sup>

The obtained values increase in the order CoZn (83.7 nm) < CoNi (97.0 nm) < NiZn (98.5 nm), respectively.



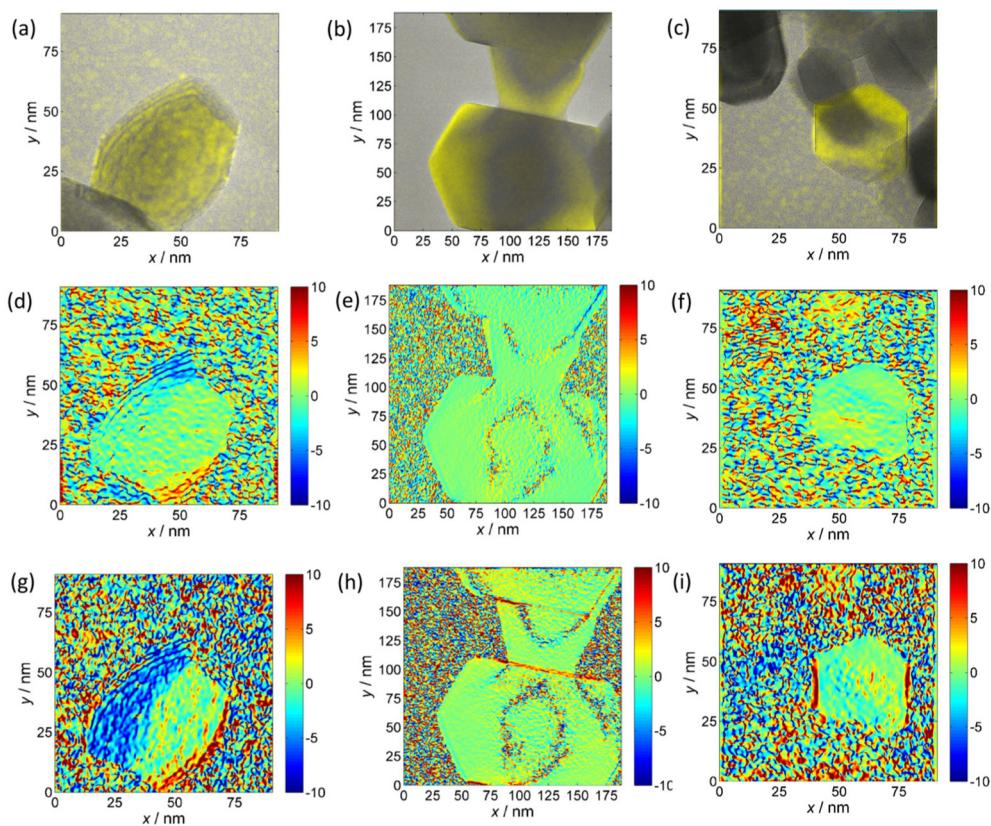


Fig. 3 Geometrical phase analysis of the NFs. (a–c) Intensity-colorized maps, (d–f) lattice rotation maps ( $^{\circ}$ ), and (g–i) lattice strain maps (% cell size). All primary particles are single crystals. The particle in panels (c, f and i) has no crystallographic relationship with its numerous neighbors whereas the particles in panels (b, e and h) are equi-oriented. The particle in panels (a, d and g) displays significant strain along its long edges that are not in contact with other particles. The shown data refer to NFs (a, d and g) CoNi, (b, e and h) CoZn and (c, f and i) NiZn.

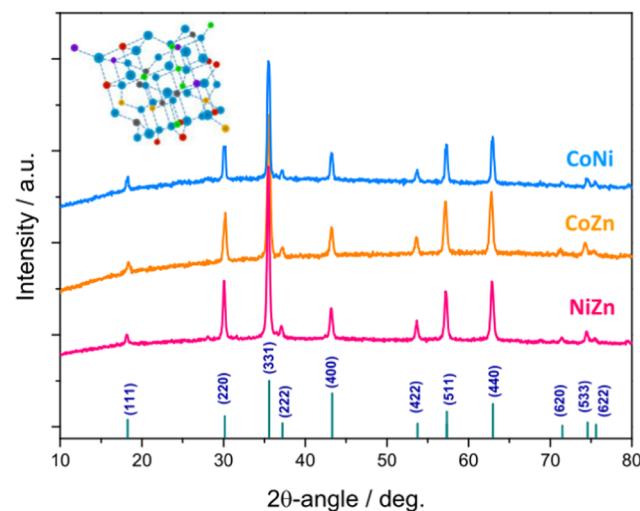


Fig. 4 XRD patterns of the HESO-NFs.

The lattice constants, as inferred from Rietveld analysis (Fig. S7, ESI<sup>†</sup>), increase in the order CoNi (8.3215(8) Å) < NiZn (8.3256(6) Å) < CoZn (8.3712(8) Å). The variation is in the same order as the average ionic radius of divalent cations (Co<sup>2+</sup>, Ni<sup>2+</sup>

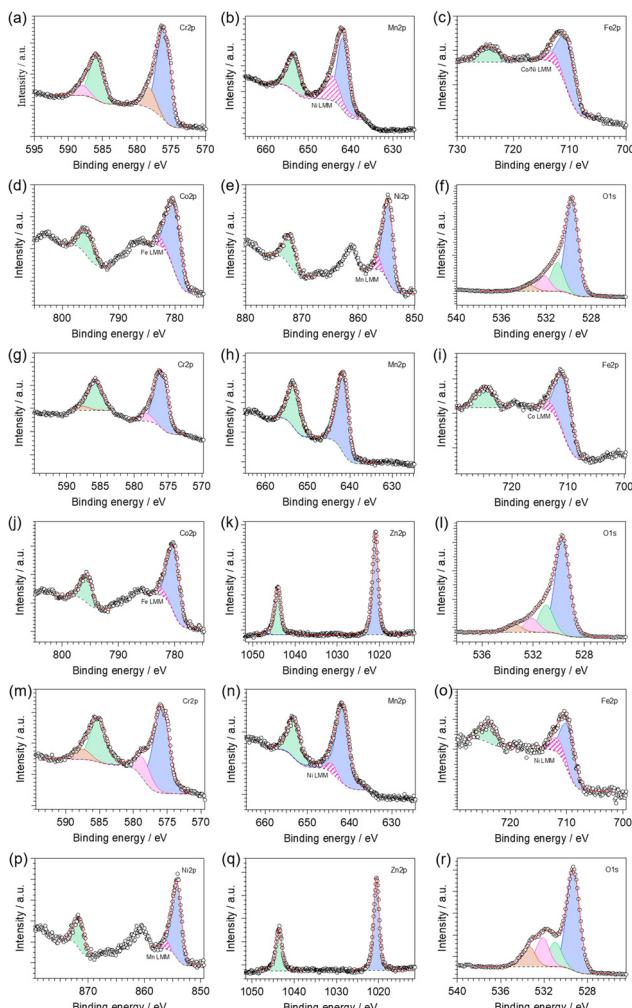
in sample CoNi, Co<sup>2+</sup>, Zn<sup>2+</sup> in sample CoZn, and Ni<sup>2+</sup>, Zn<sup>2+</sup> in sample NiZn).<sup>78,79</sup>

#### Surface composition of HESO-NFs and oxidation states of cations

Fig. S8 (ESI<sup>†</sup>) shows the X-ray photoelectron spectroscopy (XPS) survey spectra of the investigated HESO-NFs. The high-resolution X-ray photoelectron (HR-XPS) spectra of the core levels are displayed in Fig. 5. The resulting surface composition is reported in Table S3 (ESI<sup>†</sup>). In all samples, the analysis reveals that Cr, Mn, Fe and O, as well as adventitious carbon, are present on the surface. Ni and Co, Co and Zn, Ni and Zn are also detected in samples CoNi, CoZn and NiZn, respectively.

The HR-XPS spectra of Cr2p core level (Fig. 5a, g and m) are featured by two couples of spin-orbit components centered at binding energies (BEs) of *ca.* 576.0 and 578.3 eV (2p<sub>3/2</sub>) and 585.6 and 587.8 eV (2p<sub>1/2</sub>) in all samples. This indicates the presence of two different Cr-based species on the surface of the investigated materials: (i) the dominant component (see Table S4, ESI<sup>†</sup>), with its two spin-orbit features at the lower BE values, is attributed to Cr(m) species present into mixed TM spinel oxides, in accordance with the literature;<sup>80,81</sup> and (ii) the second component points to the possible presence of chromium in its high oxidation state (*i.e.*, VI).<sup>82</sup> The co-presence of Cr<sup>6+</sup> surface





**Fig. 5** High-resolution XPS spectra for samples (a–f) CoNi, (g–l) CoZn and (m–r) NiZn and deconvolution in the different spectral regions: Cr2p (a, g and m); Mn2p (b, h and n); Fe2p (c, i and o); Co2p (d and j); Ni2p (e and p); Zn2p (k and q); and O1s (f, l and r).

species has been reported also for  $(\text{Cr}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Co}_{1/5}\text{Ni}_{1/5})_3\text{O}_4$  HEO nanoparticles synthesized *via* a surfactant-assisted hydrothermal method.<sup>74</sup> It has been attributed to the oxidation of the sample surface, taking place during the 900 °C heat treatment in air.

In the Mn2p region (Fig. 5b, h and n), HR-XPS spectra reveal the presence of one type of manganese species with the characteristic two peaks as result of the spin-orbit splitting. The Mn2p<sub>3/2</sub> component is peaking at *ca.* 641.8 eV, which is closer to the BE value typical of Mn(III) rather than other oxidation states, as observed in similar materials.<sup>80</sup> In samples CoNi and NiZn, the Mn2p<sub>3/2</sub> peak overlaps with a Ni LMM Auger line (Fig. S8, ESI†).<sup>83</sup>

The HR-XPS spectra of Fe2p core level (Fig. 5c, i and o) two peaks are detected located at BEs of *ca.* 710 and 724 eV (for the 2p<sub>3/2</sub> and 2p<sub>1/2</sub> features, respectively). Interestingly, the BE values of Fe2p<sub>3/2</sub> peaks decrease in the order CoZn (710.8 eV) > CoNi (710.4 eV) > NiZn (709.8 eV); the BEs of Fe2p<sub>1/2</sub> peaks behave analogously. All these values are comprised between the

BEs of Fe(III) in  $\text{Fe}_2\text{O}_3$  and that of Fe(II) in FeO, which are typically observed at *ca.* 711.2 and 709.5 eV, respectively.<sup>80</sup> Thus, on the surface of all investigated HESO-NFs, iron is expected to be found as a mixture of both III and II oxidation states, with the former mostly present in sample CoZn, and the latter in the sample NiZn. The co-presence of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  species in spinel HEOs has been reported also by other authors.<sup>74</sup>

In CoNi, CoZn and NiZn samples, the Fe2p<sub>3/2</sub> peak overlaps with a Ni LMM and/or Co LMM Auger lines (Fig. S8, ESI†).<sup>83</sup>

In samples CoNi and CoZn, the HR-XPS spectra of Co2p core level (Fig. 5d and j, respectively) are featured by two spin-orbit components centered at BEs of *ca.* 780.2 eV (2p<sub>3/2</sub>) and 795.6 eV (2p<sub>1/2</sub>). Typically, Co(II) and Co(III) are difficult to be distinguished, due to a similar BE value at *ca.* 780.6 eV.<sup>80,83</sup> Nevertheless, the appearance of strong satellite peaks, as observed in the investigated materials, indicates that cobalt atoms are present mainly as Co(II).<sup>80,84,85</sup> The Co2p<sub>3/2</sub> peak overlaps with a Fe LMM Auger line (Fig. S8, ESI†).<sup>83</sup>

In the Ni2p region, HR-XPS spectra of samples CoNi and NiZn (Fig. 5e and p, respectively) reveal the presence of one type of nickel species with the characteristic two peaks as result of the spin-orbit splitting. The Ni2p<sub>3/2</sub> component is peaking at *ca.* 854.5 eV, which is similar to the BE value typical of Ni(II) in NiO and in mixed oxides of nickel and other metals.<sup>80</sup> In addition, the presence of satellite peaks corroborates the hypothesis that nickel atoms are present in the Ni(II) oxidation state.<sup>80,84,85</sup> The Ni2p<sub>3/2</sub> peak overlaps with a Mn LMM Auger line (Fig. S8, ESI†).<sup>83</sup>

In the Zn2p region of HR-XPS spectra of samples CoZn and NiZn (Fig. 5k and q, respectively), two strong peaks centered at *ca.* 1020.8 and 1043.9 eV appear. They are assigned to the Zn2p<sub>3/2</sub> and Zn2p<sub>1/2</sub> spin-orbit components, respectively. The observed BEs are characteristic of ZnO,<sup>86,87</sup> indicating that: (i) zinc is present as Zn(II); and (ii) apparently, zinc hydroxide is not present on the surface of these samples.

Finally, for all analyzed samples, a strong peak is observed in the O1s region (Fig. 5f, l and r). It can be decomposed in three different features (the relative amounts are reported in Table S4, ESI†). In the HR-XPS spectra of O1s core level, (i) the dominant contribution, centered at *ca.* 529.5 eV, is assigned to lattice  $\text{O}^{2-}$  ions (OL) belonging to mixed TM oxides;<sup>88–91</sup> (ii) the peak present at *ca.* 531.0 eV is attributed to native defects of  $\text{O}_2$ -vacancies (OV);<sup>88–91</sup> and (iii) the peaks centered at high BEs (*i.e.*, at *ca.* 532.1 and 533.4 eV) are associated with adsorbed or chemisorbed oxygen species, such as  $\text{O}_2$  or  $\text{H}_2\text{O}$ .<sup>92–94</sup> The fraction of OV increases in the order CoNi > NiZn ≈ CoZn (see Table S4 in ESI†), indicating that the chemical composition of the HEM can control the concentration of oxygen vacancies into the material.

#### Phase purity of the oxide and inversion degree of the spinel phase

In order to get a deeper insight into the phase purity and crystallinity of the produced HESO-NFs, micro-Raman analysis was carried out. Spectra from several random positions on each

specimen were recorded and compared to each other to evaluate the spatial homogeneity of the samples in terms of crystalline phase (Fig. S9, ESI†). The lack of significant differences in the relative intensities and shifts in the positions of the bands confirms the formation of a single oxide phase in each sample, without appreciable local deviations from the average chemical composition.<sup>71</sup>

Fig. 6 displays the averaged spectra with the apparent peak positions. According to the factor group analysis, the predicted normal vibration modes of the  $Fd\bar{3}m$  spinels ( $A_{1g} + E_g + F_{1g} + 3F_{2g} + 2A_{2u} + 2E_u + 4F_{1u} + 2F_{2u}$ ) include 39 optical modes and 3 acoustic modes.<sup>49,95–99</sup> The triply degenerate  $F_{1u}$  modes are infrared-active, whereas the  $A_{1g}$ , doubly degenerate  $E_g$  and triply degenerate  $F_{2g}$  modes are Raman-active.<sup>49,95,97,99</sup> The remaining modes are inactive.<sup>49,96</sup> All Raman-active modes involve the motions of oxygen along the cubic space diagonals.<sup>100,101</sup> The  $A_{1g}$  mode is due to the vibration along the direction joining an oxygen atom to the tetrahedral  $M^{2+}$  cation and usually appears between 600 and 720  $\text{cm}^{-1}$ .<sup>95,99,102–105</sup> The  $E_g$  mode, detected between 250 and 360  $\text{cm}^{-1}$ ,<sup>103–105</sup> is associated to symmetric bending of  $\text{O}^{2-}$  anion with respect to octahedral  $M^{3+}$  cation.<sup>103</sup> The  $F_{2g}(1)$  mode, appearing between 160 and 220  $\text{cm}^{-1}$ ,<sup>103–105</sup> originates from translation motion of  $M^{3+}\text{O}^{2-}$ , while higher frequency  $F_{2g}(2)$  and  $F_{2g}(3)$  modes, between 440 and 590  $\text{cm}^{-1}$ ,<sup>95,102–104</sup> arise from the asymmetric stretching and asymmetric bending of oxygen, respectively.<sup>104</sup>

Both positions of the Raman bands and their relative intensities strongly vary within the family of spinels.<sup>95,98,104–108</sup> Just to cite some cases, the most intense  $A_{1g}$  mode is detected at 630  $\text{cm}^{-1}$  in  $\text{ZnFe}_2\text{O}_4$  and 690  $\text{cm}^{-1}$  in  $\text{NiFe}_2\text{O}_4$ ,<sup>104</sup> the  $E_g$  mode, located at 320  $\text{cm}^{-1}$  in  $\text{NiFe}_2\text{O}_4$ , downshifts at 250  $\text{cm}^{-1}$  in  $\text{ZnFe}_2\text{O}_4$ ,<sup>104</sup> whereas the  $F_{2g}(1)$ ,  $F_{2g}(2)$  and  $F_{2g}(3)$  modes appear respectively at 180, 470 and 570  $\text{cm}^{-1}$  in  $\text{NiFe}_2\text{O}_4$  and at 160, 350 and 450  $\text{cm}^{-1}$  in  $\text{ZnFe}_2\text{O}_4$ .<sup>104</sup> In  $\text{CoFe}_2\text{O}_4$ , the  $F_{2g}(1)$ ,  $E_g$ ,  $F_{2g}(2)$ ,  $F_{2g}(3)$  and  $A_{1g}$  modes are located at 162, 302, 463, 613 and 678  $\text{cm}^{-1}$ , respectively.<sup>105</sup> In magnetite ( $\text{FeFe}_2\text{O}_4$ ), the  $F_{2g}(1)$  is

not detected, while the  $E_g$ ,  $F_{2g}(2)$ ,  $F_{2g}(3)$  and  $A_{1g}$  modes appear at 312, 474, 548 and 677  $\text{cm}^{-1}$ , respectively.<sup>95</sup>

The same occurs in  $\text{FeCr}_2\text{O}_4$ , where the  $E_g$ ,  $F_{2g}(2)$ ,  $F_{2g}(3)$  and  $A_{1g}$  modes are detected at 436, 493, 591 and 674  $\text{cm}^{-1}$ , respectively.<sup>95</sup> In  $\text{ZnCr}_2\text{O}_4$ , the  $F_{2g}(1)$ ,  $E_g$ ,  $F_{2g}(2)$ ,  $F_{2g}(3)$  and  $A_{1g}$  modes appear at 182, 452, 511, 605 and 688  $\text{cm}^{-1}$ , respectively,<sup>95</sup> whereas in  $\text{ZnMn}_2\text{O}_4$ , they are detected at 300, 321, 382, 475 and 678  $\text{cm}^{-1}$ , respectively.<sup>106</sup> As a general behavior, the band positions decrease with the increase of the radii of both octahedral and tetrahedral cations,<sup>95</sup> e.g. in aluminate spinels, the position of the  $E_g$  mode downshifts with increasing radius of tetrahedral cation (from 411  $\text{cm}^{-1}$  in  $\text{ZnAl}_2\text{O}_4$  to 395  $\text{cm}^{-1}$  in  $\text{MnAl}_2\text{O}_4$ );<sup>95</sup> the same occurs in chromites for the position of the  $F_{2g}(2)$  mode (which moves from 541  $\text{cm}^{-1}$  in  $\text{MgCr}_2\text{O}_4$  to 492  $\text{cm}^{-1}$  in  $\text{FeCr}_2\text{O}_4$ ).<sup>95</sup> As a general behavior, the band positions decrease with the increase of the radii of both octahedral and tetrahedral cations.<sup>95</sup> The partial substitution of either divalent or trivalent cations with different divalent and trivalent cations, respectively, reflects in changes (in the lattice parameters and) in the spectral profile, with shifts of the Raman peaks and variations of their relative intensities.<sup>98,107</sup> Other factors, such as the nanoparticle size<sup>108</sup> and the presence of defect-induced lattice distortions,<sup>103</sup> are also influential.

In the present case, by comparing the spectra of the three samples (Fig. 6), no marked differences in apparent positions and relative intensities of the peaks are noticed below 400  $\text{cm}^{-1}$ , which hints to a larger involvement of the trivalent cations<sup>99,101,103</sup> ( $\text{Cr}^{3+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Fe}^{3+}$ , present in all samples) in the weaker  $F_{2g}(1)$  and  $E_g$  modes. On the contrary, above 400  $\text{cm}^{-1}$ , the spectral profiles are clearly different, pointing to a greater sensitivity of the stronger  $F_{2g}(2)$ ,  $F_{2g}(3)$  and  $A_{1g}$  modes to the change in composition of the HEO-NFs (*i.e.* to the substitution of one of the divalent cations). In Ni-containing CoNi and NiZn NFs, the  $F_{2g}(2)$  mode (apparently peaking between 504 and 517  $\text{cm}^{-1}$ ) is better resolved than in CoZn NFs, where it appears as a shoulder (at  $\sim 500 \text{ cm}^{-1}$ ), while the most intense  $A_{1g}$  mode, lying in the frequency range (620–700  $\text{cm}^{-1}$ ) peculiar to ferrites and chromites,<sup>102,104</sup> apparently peaks at 658  $\text{cm}^{-1}$  in NiZn NFs and at lower frequencies (633 and 620  $\text{cm}^{-1}$ ) in CoZn and CoNi NFs. In the latter sample, a shoulder further appears on the higher frequency side of the  $A_{1g}$  mode, suggesting the occurrence of inversion,<sup>71,95,109</sup> in agreement with what reported for  $(\text{Cr}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Co}_{1/5}\text{Ni}_{1/5})_3\text{O}_4$  nanoparticles, prepared *via* sol-gel method<sup>43</sup> and reverse co-precipitation approach.<sup>76</sup>

To ensure electroneutrality of the 2–3 spinel  $\text{M}_3\text{O}_4$  phase, 1/3 of the cations must have charge +2 and 2/3 must have charge +3. Considering the relative stability of  $\text{M}^{2+}$  and  $\text{M}^{3+}$  cations in the spinel oxide lattice it is expected that chromium and zinc are present as  $\text{Cr}^{3+}$  and  $\text{Zn}^{2+}$ , respectively. The other cations (Mn, Fe, Co, Ni) can occur as both  $\text{M}^{2+}$  and  $\text{M}^{3+}$ . The preference for  $\text{M}^{3+}$  decreases as  $\text{Mn} > \text{Fe} > \text{Co} > \text{Ni}$ .

In spinel oxides, cations occupy tetrahedral 8a sites and octahedral 16d sites (Fig. S1, ESI†). The energy difference between the 8a and 16d site for middle-late 3d ions ranges from 0 ( $\text{d}^5$  and  $\text{d}^{10}$  ions) to 158  $\text{kJ mol}^{-1}$  ( $\text{d}^3 \text{Cr}^{3+}$ ).<sup>110,111</sup> This explains why ferrites  $\text{MFe}_2\text{O}_4$  are often inverse ( $\text{Fe}^{3+}$  is  $\text{d}^5$ ), while

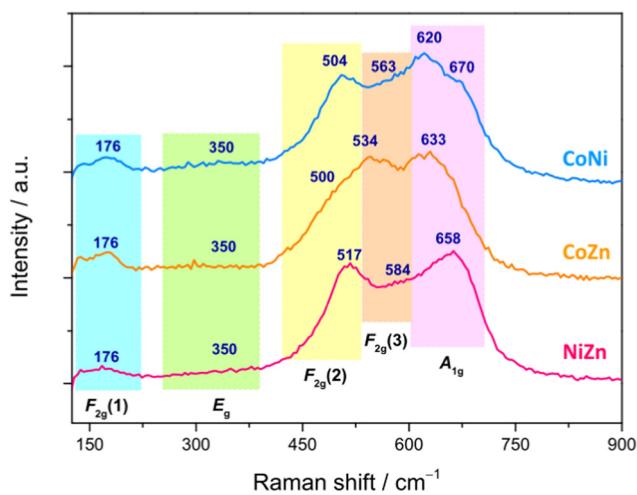


Fig. 6 Averaged micro-Raman spectra of the HESO-NFs (the apparent peak positions, in  $\text{cm}^{-1}$ , are also reported).



chromites  $\text{MCr}_2\text{O}_4$  are always normal.<sup>112</sup> Clearly, TEM is not able to resolve the 8a and 16d sites, so one may wonder whether entropic effects are strong enough to overcome the cation site preferences and achieve uniform cation distribution over all sites, or uniform distribution only occurs within 8a and 16d sites separately, leaving room to satisfy the cation site preferences. Using the crystal-field-theory based values for the octahedral stabilization energy<sup>110</sup> and adapting the formula for the configurational entropy<sup>113</sup> of a crystal with sublattice to the spinel structure as

$$S_{\text{config}}^{\text{FU}} = -R \left( \sum_i x_i^{(8a)} \ln x_i^{(8a)} + 2 \sum_i x_i^{(16d)} \ln x_i^{(16d)} \right) \quad (1)$$

where the configurational entropy is calculated for a formula unit (FU)  $\text{M}_3\text{O}_4$ ,  $x_i^{(8a)}$  and  $x_i^{(16d)}$  are the fractions of metal  $i$  occupying the 8a and 16 sites, respectively, we can estimate the Helmholtz free energy  $F^{\text{FU}}$  corresponding to a given distribution of cations. The distributions are strongly favored that have cations (i) partitioned between 8a and 16d sites to optimize octahedral stabilization, and (ii) randomly distributed within the 8a and 16d sites, under the electroneutrality constraint. At 1173 K (our highest calcination temperature), the cation distributions detailed in Table 1 have  $F^{\text{FU}}$  lower than that of the completely random distribution by 37 to 45 kJ mol<sup>-1</sup> (the details of the calculations can be found in the ESI†). The occurrence of intrasite-random cation distributions is consistent with the presence of Mn as  $\text{Mn}^{3+}$ , Fe as a mixture of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ , and of Co mostly as  $\text{Co}^{2+}$ , evidenced by the XPS data. It also agrees with the XAS data for  $(\text{Co}_{1/5}\text{Mg}_{1/5}\text{Mn}_{1/5}\text{Ni}_{1/5}\text{Zn}_{1/5})-(\text{Al}_{1/5}\text{Co}_{1/5}\text{Cr}_{1/5}\text{Mn}_{1/5})_2\text{O}_4$ ,<sup>114</sup> and the XANES data for  $(\text{Ti}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Co}_{1/5}\text{Ni}_{1/5})_3\text{O}_4$ ,<sup>115</sup> which indicate that the cation site preferences are satisfied. Very recently, Sarkar *et al.*<sup>65</sup> demonstrated that micrometer-sized  $(\text{Cr}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Co}_{1/5}\text{Ni}_{1/5})_3\text{O}_4$  HESO has intrasite-random cation distribution with  $(\text{Co}_{3/5}\text{Fe}_{2/5})$  in 8a sites and  $(\text{Cr}_{3/5}\text{Mn}_{3/5}\text{Fe}_{1/5}\text{Ni}_{3/5})$  in 16d sites using X-ray, Mössbauer, and neutron techniques. They also expect that Cr and Fe are present as trivalent cations, Ni as divalent cation, and Mn and Co as a mixture of  $\text{M}^{2+}$  and  $\text{M}^{3+}$  ( $\text{M}^{2+}/\text{M}^{3+} = 10:90$  for Mn, 60:40 for Co). The important role of the excess octahedral stabilization was recognized, as we independently did. The data are close to those in Table 1. So, we are confident that the cation

**Table 1** Cation distributions that satisfy electroneutrality and optimize octahedral stabilization

NF	Site	$\text{M}^{2+}$	$\text{M}^{3+}$	$\lambda^a$ (%)
CoNi	8a	$\text{Co}_{1/5}$	$\text{Fe}_{3/5}\text{Co}_{1/5}$	80
	16d	$\text{Ni}_{3/5}\text{Co}_{1/5}$	$\text{Cr}_{3/5}\text{Mn}_{3/5}$	
CoZn	8a	$\text{Zn}_{3/5}$	$\text{Fe}_{2/5}$	40
	16d	$\text{Co}_{2/5}$	$\text{Cr}_{3/5}\text{Mn}_{3/5}\text{Fe}_{1/5}\text{Co}_{1/5}$	
NiZn	8a	$\text{Zn}_{3/5}$	$\text{Fe}_{2/5}$	40
	16d	$\text{Ni}_{2/5}$	$\text{Cr}_{3/5}\text{Mn}_{3/5}\text{Fe}_{1/5}\text{Ni}_{1/5}$	

<sup>a</sup> Inversion degree, defined as the fraction of trivalent cations in the 8a sublattice.

distributions we propose for  $(\text{Cr}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Co}_{1/5}\text{Zn}_{1/5})_3\text{O}_4$  and  $(\text{Cr}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Ni}_{1/5}\text{Zn}_{1/5})_3\text{O}_4$  are close to the true ones.

In order to infer additional information, Gaussian bands were utilized to reproduce the micro-Raman spectra (Fig. S10, ESI†). Besides the  $\text{F}_{2g}(1)$ ,  $\text{E}_g$ ,  $\text{F}_{2g}(2)$ ,  $\text{F}_{2g}(3)$  and  $\text{A}_{1g}$  modes, additional bands were found to contribute to the Raman intensity, confirming that inversion occurs, to different extent, in all samples.<sup>71,76,95,109</sup>

## Magnetic properties

**General considerations.** It is clear from the preceding discussion that the interpretation of the magnetic data will benefit from reference to chromites, manganites, and ferrites with spinel structure.

The primary particles comprising the HESO-NFs have diameter from a few tens of nm to the hundred nm range. From XRD data, the average crystallite diameter is  $\approx 100$  nm for CoNi and NiZn and  $\approx 85$  nm for CoZn. Magnetic lengths, such as the single-domain, coherent rotation, and superparamagnetic (SPM) blocking diameters,<sup>116</sup> are a useful (though approximate) starting framework to develop the interpretation of magnetic data. We could find in the literature data for  $\text{Fe}_3\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$ , and  $\text{CoCr}_2\text{O}_4$  (Table S8, ESI†). The NF primary particles have diameter similar to the single-domain diameter of  $\text{Fe}_3\text{O}_4$  and much smaller than that of  $\text{CoFe}_2\text{O}_4$  and  $\text{CoCr}_2\text{O}_4$ , so they reasonably comprise a single domain. Magnetization inversion by coherent rotation diameter is expected if the NF behave as chromites but partially incoherent inversion (e.g., curling) might occur if the NFs behave similarly to ferrites. Finally, the NF primary particles are much larger than the SPM blocking diameter at 400 K of all three spinel oxides and, therefore, superparamagnetism is not expected to be important.

**Magnetic data and analysis.** The high field magnetization  $M_{50k}$  ( $H = 50$  kOe) and remanence  $M_{\text{rem}}$  were measured between 5 and 300 K (Fig. 7). All samples have significant high-field and remanent magnetization, at least at low temperature, and are thus able to sustain a magnetically ordered structure.  $M_{50k}$  and  $M_{\text{rem}}$  at 5 K are in the 17–40 emu g<sup>-1</sup> and 10–30 emu g<sup>-1</sup> range, respectively, that correspond to molar magnetization per formula unit (FU) in the range 0.7–1.7  $\mu_{\text{B}}$  and 0.4–1.3  $\mu_{\text{B}}$ , respectively ( $\mu_{\text{B}}$  is the Bohr magneton). Since the cations, except  $\text{Zn}^{2+}$ , have molar magnetization in the 3.2–5.9  $\mu_{\text{B}}$  range, the measured  $M_{50k}$  and  $M_{\text{rem}}$  demonstrate that the NFs have an ordered magnetic structure of ferrimagnetic (FIM) nature, excluding ferromagnetic (FM) and (canted) antiferromagnetic (AFM) structures, which would display much larger and smaller  $M_{50k}$  and  $M_{\text{rem}}$ , respectively. The squareness  $M_{50k}/M_{\text{rem}}$  is large at 5 K, it extrapolates to  $\approx 0.75$  at 0 K, a value typical of Stoner-Wohlfarth particles with cubic anisotropy. Incoherent magnetization inversion and interparticle interactions seem thus to be relatively unimportant even at low temperature.<sup>117</sup>

The magnetization for a completely collinear FIM structure, such as that found in the mixed ferrites  $\text{MFe}_2\text{O}_4$ , can be calculated by a Monte Carlo approach based on Table 1. The calculated values are 2.5, 7.0, 6.3  $\mu_{\text{B}}$  per FU for CoNi, CoZn and NiZn NFs, respectively. Thus, the observed magnetization is not



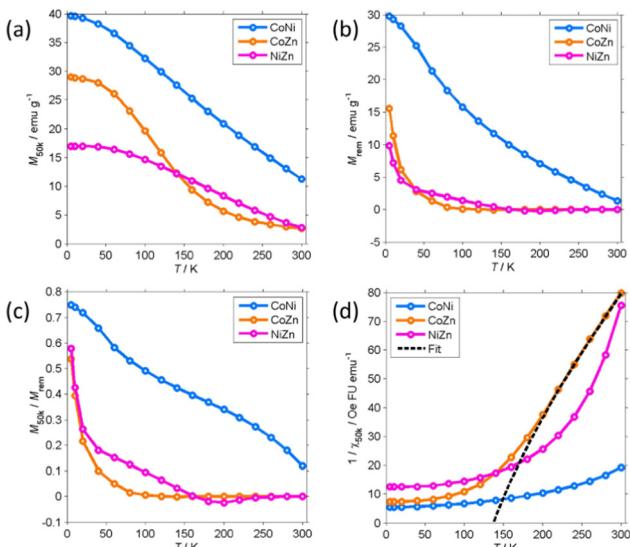


Fig. 7 Temperature dependence of the high field magnetization  $M_{50k}$  (a,  $H = 50$  kOe), remanence  $M_{rem}$  (b), squareress  $M_{50k}/M_{rem}$  (c), and inverse high-field susceptibility  $1/\chi_{50k}$  (d) of the NFs. The dashed line in panel (d) is the best-fit Curie-Weiss-Néel curve for CoZn NFs.

consistent with a collinear, antiparallel alignment of the ionic magnetic moments (sublattice magnetizations), like in the typical Néel FIM structure. It is however consistent with a FIM structure where the sublattice magnetizations are not collinear.

$M_{50k}$  and  $M_{rem}$  decrease with increasing temperature.  $M_{rem}$  of CoNi at 300 K (1.35 emu g<sup>-1</sup>) is 5% of the remanence at 5 K. The remanence of Zn-containing (CoZn and NiZn) NFs vanishes well below RT. Therefore, CoZn and NiZn NFs are paramagnetic (PM) at 300 K and CoNi NFs probably becomes PM slightly above RT.

We now turn our attention to the transition temperature  $T_C$  between the FIM and PM phases. Considering that the primary particles have size ranging from a few tens of nm to the hundred nm range, we expect a distribution of transition temperatures. The temperature, at which  $M_{rem}$  vanishes, marks the  $T_C$  of the primary particles with highest  $T_C$ , presumably the largest particles. Due to noise and artifacts, it is not possible to accurately measure where  $M_{rem}$  vanishes. The best estimate is that  $T_C \approx 150$  and 200 K for CoZn and NiZn NFs, respectively. This ordering of the  $T_C$  = (CoNi > NiZn > CoZn) can also be appreciated in the  $M_{50k}$  plot (Fig. 7).  $M_{50k}$  of CoZn changes concavity at  $\approx 150$  K, suggesting that at higher temperatures it follows the Curie-Weiss-Néel law for ferrimagnets,<sup>112</sup>

$$\frac{1}{\chi} = \frac{T}{C} + \frac{1}{\chi_0} - \frac{\sigma}{T - \theta_p} \quad (2)$$

where  $\chi = M/H$  is the susceptibility,  $C$  is the Curie constant,  $\chi_0$  and  $\sigma$  are related to the intra- and inter-sublattice molecular fields, and  $\theta_p$  is the paramagnetic Curie point, which is slightly higher than the true transition temperature  $T_C$ .<sup>118</sup> As can be seen in Fig. 7d,  $1/\chi_{50k}$  of CoZn closely follows the Curie-Weiss-Néel law for  $T > 200$  K, so we can identify the PM and FIM

Curie points  $T_C \approx \theta_p = 137$  K, in agreement with  $T_C$  from  $M_{rem}$  data. Interestingly, the asymptotic temperature  $\theta_N = -C/\chi_0$  is close to zero, indicating the presence of frustrated FM and AFM exchange interactions that compete and partly compensate.<sup>119</sup> The Curie constant corresponds to an effective moment  $\mu_{eff} = (3k_B C/N_A) = 5.0\mu_B$  per FU that is just 66% of that calculated by a Monte Carlo approach. This discrepancy is probably due to the lack of data in the high temperature range where the  $T/C$  term of eqn (2) is dominant.

Confirmation of the presence of a FIM-PM transition and details about the FIM phase are provided by the magnetization isotherms  $M(H)$  measured at different temperature (Fig. 8). Since the magnetization is not always saturated at 50 kOe, we analyzed how  $M$  approaches saturation<sup>117</sup> to more accurately estimate the true  $M_{sat}$ .

The magnetic parameters are collected in Table 2 (see Experimental section in ESI† for details).

The behavior of the NFs is markedly different from each other. The CoNi NFs have open loops that do not change shape up to 300 K. At low  $T$ , the coercivity  $H_c$  is moderate (0.83 kOe). On increasing temperature,  $M_{sat}$ ,  $M_{rem}$ ,  $H_c$ , and the coercivity of the remanence  $H_{cr}$  decrease slowly due to the approach to the

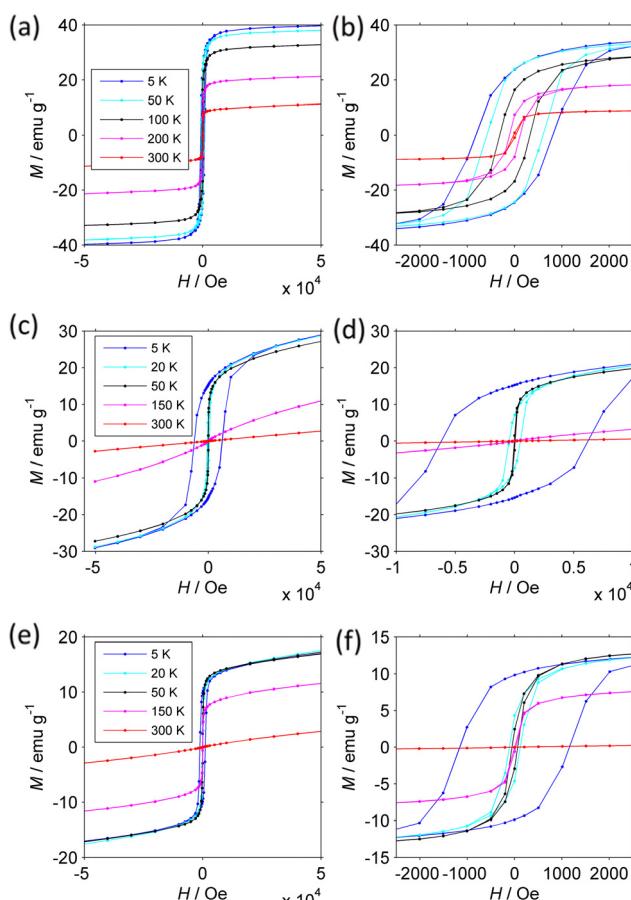


Fig. 8 Magnetization isotherms  $M(H)$  of the (a and b) CoNi, (c and d) CoZn and (e and f) NiZn NFs. The panels (b, d and f) show the central part of the isotherms. Note the different horizontal scale of the panel (d).



critical FIM-PM  $T_C$ . This interpretation is supported by the large size of the primary particles and the dependence of coercivity on  $T$ . Indeed, neither  $H_c$  nor  $H_{cr}$  follow Kneller's law<sup>120</sup> typical of thermally activated magnetization inversion process. They instead follow a power law  $(H_c/H_{c,0}) \approx (M_{sat}/M_{sat,0})^{4.5}$ , where the 0 subscript indicates the value at 5 K, which, provided that  $H_c$  is proportional to the anisotropy field  $2 \text{ K}/M_{sat}$ , is consistent with Zener's law<sup>121</sup> typical of bulk materials. Further supporting evidence will be provided below.

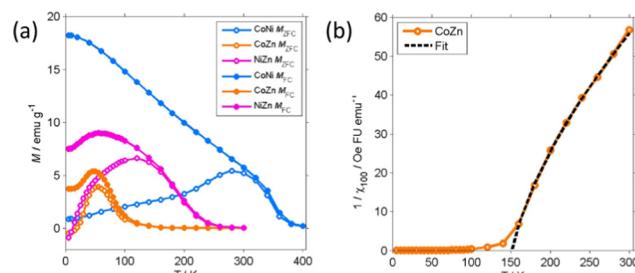
The magnetization isotherms of CoZn and NiZn NFs have similar behavior though at shifted temperature mirroring the different  $T_C$ . From 5 to 150 K, they are open loops with almost constant  $M_{sat}$  and dramatically decreasing  $H_c$  (and  $H_{cr}$ ). The main difference is that CoZn NFs have much larger  $H_c$  at 5 K (6.37 kOe) than NiZn NFs have (1.17 kOe). It is noteworthy that CoNi NFs have  $H_c$  lower than that of CoZn NFs, despite the presence of Co in both NFs. This difference can be attributed to the fact that in CoZn NFs a larger fraction of Co is present in octahedral 16d sites (see Table 1). At 150 K, the magnetization of NiZn NFs still is non-linear, while that of CoZn NFs is almost linear. At 300 K, both NFs are definitely in a linear regime: at  $H = 50$  kOe, the paramagnetic magnetization  $M_p = \chi_p H$  is 83% and 99% of the total  $M_{50\text{K}}$  magnetization for NiZn and CoZn NFs, respectively.  $M_p$  is truly related to primary particles that have entered the PM regime, as shown by the small magnitude of its slope  $\chi_p$ , which corresponds to a magnetization of a few  $\mu_B$  per FU. In the SPM regime, the initial susceptibility would be several orders of magnitude larger and strong non-linearity would be observed already at  $H < 1$  kOe.

Temperature dependent  $M(H)$  curves have thus strengthened the conclusion that our HESO-NFs have a low- $T$  FIM phase and a high- $T$  PM phase with transition temperature  $T_C$  decreasing as CoNi > NiZn > CoZn. They have provided further evidence that SPM effects are not dominant, as

**Table 2** Magnetic parameters of the NFs calculated from the magnetization isotherms  $M(H)$ . Parameters may be absent when the NFs are mostly paramagnetic

	$T$ (K)	$M_{sat}^a$ (emu g <sup>-1</sup> )	$M_{rem}$ (emu g <sup>-1</sup> )	$M_{rem}/M_{sat}$	$H_c$ (kOe)	$H_{cr}$ (kOe)	$10^4 \chi_p$ (emu g <sup>-1</sup> Oe <sup>-1</sup> )
CoNi	5	39.3	24.1	0.61	0.82	0.94	0.15
	50	37.4	24.2	0.64	0.59	0.70	0.18
	100	31.9	16.6	0.52	0.32	0.35	0.22
	200	20.0	7.6	0.38	0.11	0.14	0.28
	300	9.6	0.9	0.09	0.02		0.36
CoZn	5	27.9	15.3	0.55	6.37	6.77	0.72
	20	23.4	7.2	0.31	0.48	0.68	1.23
	50	21.8	1.97	0.09	0.04	0.04	1.22
	150	3.68	0.02	0.006	0.03		1.55
	300						0.54
NiZn	5	14.8	9.86	0.65	1.17	1.30	0.51
	20	14.7	4.47	0.30	0.12	0.17	0.62
	50	14.6	2.69	0.18	0.06	0.09	0.57
	150	9.6	0.35	0.04	0.01		0.44
	300	0.7			0.01		0.45

<sup>a</sup>  $M_{sat}$  is the saturation magnetization as obtained from the analysis of the approach to saturation.<sup>117</sup>



**Fig. 9** Temperature dependence of the low-field (100 Oe) magnetization of the NFs. Left: ZFC and FC magnetization of the NFs. Right: Inverse low-field susceptibility  $1/\chi_{100}$  of CoZn NFs. The dashed line is the best-fit Curie–Weiss–Néel curve for CoZn NFs.

anticipated on the basis of the size of the primary particles. The small  $\chi_p$ , corresponding to a FU magnetization of a few  $\mu_B$ , is consistent with a non-collinear FIM structure.

More detailed information about the magnetic structure of the NFs is obtained from the zero-field cooled (ZFC) and field cooled (FC) magnetization ( $M_{ZFC}$ ,  $M_{FC}$ ) measured with  $H_{cool} = H_{meas} = 100$  Oe (Fig. 9). All (Z)FC curves differ from the typical (Z)FC curves of ferrite NPs.

For instance, the ZFC–FC bifurcation occurs at temperature much higher than the maximum  $M_{ZFC}$ . The NFs display (Z)FC curves with similar shape that have different temperature span in correspondence to the unequal  $T_C$ . Extending the temperature range up to 400 K allowed us to observe the transition of CoNi NFs to the PM phase. There clearly is a dispersion of the transition temperature due to the particulate nature of the NFs.

Therefore, to estimate  $T_C$  from  $M_{FC}$  data, the intercept of the maximum slope line was extrapolated and its intersection with the  $M = 0$  axis was interpreted as an average  $T_C$ . For CoNi NFs, the FIM-PM transition occurs at  $T_C = 374$  K (Table 3). On decreasing  $T$ ,  $M_{FC}$  increases almost linearly and then levels off at  $T \leq 20$  K. No low  $T$  transition is observed. The  $M_{FC}$  of CoNi NFs is almost exactly proportional to  $M_{50\text{K}}$  ( $M_{FC} \approx 0.44M_{50\text{K}}$ ) showing that there is a common thermal process underlying the  $M$  increase at low  $T$ . This process is the thermal dealignment of the spins about the magnetization axis. Thermally activated magnetization inversion (superparamagnetism) can be excluded since it strongly depends on the applied field. The large difference between  $M_{ZFC}$  and  $M_{FC}$  may be related to several causes.

It can be due to the presence of sizeable magnetic anisotropy typical of spinel oxides. The power dependence of  $H_c$  on  $M_{sat}$  supports this hypothesis. Another possible explanation is the

**Table 3** Critical temperatures of the NFs<sup>a</sup>

NF	$T_C$ (K)	$T_S$ (K)
CoNi	374	
CoZn	105	20
NiZn	233	11

<sup>a</sup> Estimated from the intercept of the maximum slope line with the  $M = 0$  axis ( $T_C$ ) or  $M = M(5\text{ K})$  line ( $T_S$ ).



formation of a spin-glass-like phase below RT. This seems less likely, at least for CoNi, as  $M_{ZFC}$  and  $M_{FC}$  are already unequal at RT.

The (Z)FC magnetization of Zn-containing NFs is close to zero at RT and rapidly increases when the transition to the FIM phase approaches. The PM phase gives way to a FIM phase at  $T_C = 233$  (NiZn) and 105 K (CoZn), temperatures much lower than that of CoNi NFs.  $M_{FC}$  reaches a maximum at 50 K and then decreases and levels off at low  $T$ . This marks the transition to a phase with lower  $M$  at the (average) critical temperature  $T_S = 11$  and 20 K for NiZn and CoZn NFs, respectively. The  $M$  decrease suggests the formation of a spin-glass-like phase. The shape of  $M_{ZFC}$  does not allow us to exclude SPM phenomena, but the thermal unblocking of the spin-glass-like phase and the thermal decrease of  $M_{sat}$  (clearly observed in the CoNi NFs) seems sufficient to explain the temperature dependence of  $M_{ZFC}$ . Therefore, the (Z)FC magnetization of Zn-containing NFs gives evidence of the occurrence of another magnetic structure at very low  $T$ .

The low-field susceptibility  $\chi_{100} = M_{FC}/H_{meas}$  sufficiently extends above  $T_C$  to be significantly modelled by the Curie-Weiss-Néel law (eqn (2)) only for the CoZn NFs.  $1/\chi_{100}$  closely follows eqn (2) for  $T > 150$  K (Fig. 9). The asymptotic temperature  $\theta_N \approx 0$  and the effective moment  $\mu_{eff} = 6.1\mu_B$  (80% of  $\mu_{eff}$  calculated by a Monte Carlo approach) are both in agreement with the results of the modelling of  $1/\chi_{50K}$ . The best-fit parameters provide  $T_C \approx \theta_p = 150$  K, in agreement with  $M_{rem}$  data and the modeling of the high-field susceptibility. This  $T_C$  is not inconsistent with that in Table 3 since the former is the  $T_C$  of the largest particles while the latter represent an average over all particles.

## Discussion of the magnetic properties and structure

As anticipated, the magnetic results can be discussed with reference to the magnetic structure of ferrites, chromites, and manganites. The magnitude of  $M_{sat}$  and the temperature dependence of  $M_{(Z)FC}$  and  $H_c$  are not consistent with the usual behavior of ferrites, which have Néel FIM phases with collinear sublattice magnetization and  $T_C$  above  $\approx 600$  K. It is also interesting to note that when Zn replaces a magnetic cation (Co, Ni) in our NFs, the magnetization decreases, at variance with ferrites that show the well-known magnetization increase upon Zn substitution.<sup>122</sup>

In spinel-structure chromites  $MCr_2O_4$  and manganites  $MMn_2O_4$ , the interplay between strength and frustration of the superexchange interactions is such that they display a non-collinear FIM phase with  $M_{sat}$  and  $T_C$  much lower than those of corresponding ferrites  $MFe_2O_4$ , and often a transition ( $T_S$ ) to a low temperature reentrant spin-glass-like phase.<sup>119</sup> The magnetic structure of the low- $T$  phase in chromites typically is conical/spiral with a long-range ordered longitudinal component and a short-range (a few nm) ordered transverse component.<sup>123-125</sup> The low- $T$  phase of manganites has been less studied. The neutron diffraction data of  $NiMn_2O_4$  at  $T = 1.5$  K were interpreted in terms of a strongly canted magnetic structure where the sublattice magnetizations form an angle of 27°.

The magnetic behavior of Zn-containing CoZn and NiZn NFs closely resembles that of chromite (and manganites) under

many respects. For instance, the dramatic decrease of coercivity at low  $T$  indicates the transition between the spin-glass-like and the non-collinear FIM phase.<sup>126</sup> Therefore, the magnetic behavior of CoZn and NiZn NFs is consistent with the presence of an intermediate non-collinear FIM phase and a low- $T$  reentrant spin-glass-like phase. The CoNi NFs share some magnetic characteristic with chromites, *e.g.*, the low  $M_{sat}$ , but under other respects, *e.g.*, the relatively high  $T_C$  and the slow decrease of  $M_{sat}$ ,  $M_{rem}$ , and  $H_c$  with increasing  $T$ , they behave like a ferrite. This behavior can be understood with reference to the parameter  $u$ ,<sup>126</sup> which quantifies the magnetic frustration:

$$u = (4J_{BB}S_B)/(3J_{AB}S_A) \quad (3)$$

where  $J_{AB}$  is the superexchange integral between the nearest-neighbor spins at the 8a and 16d sites,  $J_{BB}$  is that between the nearest-neighbor spins at two 16d sites, and  $S_A$  and  $S_B$  are the magnitudes of the spins at the 8a and 16d sites. For small  $u$  ( $< 8/9$ ), Néel collinear FIM structure occurs, but at larger  $u$  the increasing frustration gives rise to non-collinear FIM structures with decreasing order range.<sup>123</sup> In CoNi the full network of superexchange interactions counteracts the magnetic frustration and the effects of the latter are weaker than those in  $MCr_2O_4$  and  $MMn_2O_4$  spinel oxides. The replacement of a magnetic cation by  $Zn^{2+}$  in CoZn and NiZn NFs significantly reduces the average values of both  $J_{AB}$  and  $S_A$ , leading to a lower  $T_C$ , and it increases  $u$  and the magnetic frustration, leading to lower collinearity and the occurrence of a reentrant spin-glass-like-phase at low  $T$ .

The above argument about magnetic structure is based on the close similarities of the chemical composition, crystal structure, and magnetic behavior between our HESO NFs and the spinel oxides chromites, manganites, and ferrites. Of course, we do not claim that we have proved the HESO NF magnetic structure, which would require additional experiments, such as magnetic neutron scattering, that are outside the scope of this paper. It however seems more likely that, for compounds of identical crystal structure and similar chemical composition, similar magnetic behavior stems from similar magnetic structure than that different magnetic structures accidentally give rise to similar magnetic behavior. Caution is however in order as HE compounds might display properties far from those of the corresponding low-entropy compounds.

Finally, we compare our results with preceding magnetic characterization of HESOs. The magnetic properties of HESOs have already been summarized.<sup>59,60</sup> Spinel oxides with composition  $(Cr_{1/5}Mn_{1/5}Fe_{1/5}Co_{1/5}Ni_{1/5})_3O_4$ , equal to that of CoNi NFs, have attracted some attention. The literature magnetic data (Table 4) are in general agreement with those recorded for our CoNi NFs but they were rarely discussed in detail. Magnetization isotherms were first measured on NP aggregates obtained by solution combustion followed by calcination.<sup>64,127</sup> The  $M(H)$  curves at RT were slightly open loops similar to that of CoNi NFs.  $M(H)$  at 300 K was also measured on aggregates of  $\approx 100$  nm particles synthesized by a sol-gel procedure, and in this case a closed  $M(H)$  curve typical of SPM behavior was recorded.<sup>63</sup> A more in-depth investigation of bulk  $(Cr_{1/5}Mn_{1/5}Fe_{1/5}Co_{1/5}Ni_{1/5})_3O_4$  obtained by sintering at 1273 K was later reported.<sup>65</sup> The results



Table 4 Magnetic parameters of HESOs from the literature

	<i>T</i> (K)	High-field <i>M</i> (emu g <sup>-1</sup> )	<i>M</i> <sub>rem</sub> (emu g <sup>-1</sup> )	<i>H</i> <sub>c</sub> (kOe)	<i>T</i> <sub>C</sub> (K)	Ref.
$(\text{Cr}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Co}_{1/5}\text{Ni}_{1/5})_3\text{O}_4$	RT	16.0 <sup>a</sup>	3.8 2.5 21 0.51 0.02 0.20 0.23	0.06	127 64 63 65 62 65 $> 380$ K 65	
	RT	9.9 <sup>b</sup>		0.18		
	300	16 <sup>c</sup>				
	4	44 <sup>d</sup>				
	300	13.2 <sup>c</sup>				
	50	35.3 <sup>c</sup>				
	300	41.1 <sup>g</sup>				
	5	15.9 <sup>g</sup>				
$(\text{Cr}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Co}_{1/5}\text{Zn}_{1/5})_3\text{O}_4$	RT	8.1 <sup>b</sup>	0.8	0.06	64	
$(\text{Cr}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Ni}_{1/5}\text{Zn}_{1/5})_3\text{O}_4$	RT	5.6 <sup>b</sup>	0.6	0.09		

<sup>a</sup> At 20 kOe. <sup>b</sup> At 30 kOe. <sup>c</sup> At 5 kOe. <sup>d</sup> At 90 kOe. <sup>e</sup> From magnetization data. <sup>f</sup> From Mössbauer data. <sup>g</sup> At 40 kOe.

from Mössbauer and magnetometric data, including the FIM-PM *T*<sub>C</sub>, are very similar to those of CoNi NFs. A broad investigation of high-entropy spinel oxides  $\text{M}_3\text{O}_4$ , ferrites  $\text{MFe}_2\text{O}_4$ , and chromites  $\text{MCr}_2\text{O}_4$  has been reported upon, which includes  $(\text{Cr}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Co}_{1/5}\text{Ni}_{1/5})_3\text{O}_4$ , spinel oxide.<sup>62</sup> The HEOs were synthesized by ball milling, compression, and sintering at 1523 K. The *M(H)* isotherms (5–300 K) of  $(\text{Cr}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Co}_{1/5}\text{Ni}_{1/5})_3\text{O}_4$  are consistent with the present data for CoNi NFs, but the *M*<sub>ZFC</sub> and *M*<sub>FC</sub> curves are rather different. The latter have a shape loosely similar to the curves in Fig. 9, but they are quantitatively very different, *e.g.*, *M*<sub>FC</sub> (5 K, *H*<sub>cool</sub> = *H*<sub>meas</sub> = 100 Oe) for the bulk HESO (6.6 emu g<sup>-1</sup>) unexpectedly is much lower than that of CoNi NFs (18.2 emu g<sup>-1</sup>). The magnetic data was explained in terms of the occurrence of Cr or Mn rich regions with AFM structure. We think that the behavior of  $(\text{Cr}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Co}_{1/5}\text{Ni}_{1/5})_3\text{O}_4$  HESO is better explained on the basis of the presence of Cr and Mn, reasonably as Cr<sup>3+</sup> and Mn<sup>3+</sup> in the 16d sites. Indeed, in the same paper the ZFC-FC curves of high-entropy chromites  $\text{MCr}_2\text{O}_4$  are displayed, which closely resemble those of the CoZn and NiZn NFs and confirm that frustration effects are induced by Cr and increased by the replacement of magnetic cations by non-magnetic ones. Finally, micrometer-sized  $(\text{Cr}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Co}_{1/5}\text{Ni}_{1/5})_3\text{O}_4$  particles were recently studied.<sup>65</sup> The 300 K isotherm is reversible whereas at 5 K a small coercivity (0.23 kOe) was observed. These data agree with those here measured for CoNi NFs, the coercivity difference is explained by the larger size of the particles, which are multidomain (see Table S8, ESI†). The (Z)FC magnetization is similar to the present one except for an inflection at  $\approx 75$  K, which was attributed to the depinning of domain walls.

HESOs with composition equal to CoZn and NiZn NFs have been much less studied.<sup>64</sup> The RT *M(H)* curves of aggregates of 24 nm NPs, obtained by solution combustion followed by calcination, were slightly open loops (*H*<sub>c</sub> < 0.1 kOe) in stark contrast with CoZn and NiZn NFs, which are essentially PM at RT. We can only speculate that this striking difference is due to the different synthetic route and morphology of the oxides.

## Conclusions

Electrospun  $(\text{Cr}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Co}_{1/5}\text{Ni}_{1/5})_3\text{O}_4$ ,  $(\text{Cr}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Co}_{1/5}\text{Zn}_{1/5})_3\text{O}_4$  and  $(\text{Cr}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Ni}_{1/5}\text{Zn}_{1/5})_3\text{O}_4$  NFs, exhibit porous

structure consisting of interconnected nearly strain-free oxide single crystals with pure  $Fd\bar{3}m$  spinel structure. The in-depth investigation of their magnetic properties shows that  $(\text{Cr}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Co}_{1/5}\text{Ni}_{1/5})_3\text{O}_4$ ,  $(\text{Cr}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Co}_{1/5}\text{Zn}_{1/5})_3\text{O}_4$  and  $(\text{Cr}_{1/5}\text{Mn}_{1/5}\text{Fe}_{1/5}\text{Ni}_{1/5}\text{Zn}_{1/5})_3\text{O}_4$  NFs have a diverse and rich magnetic behavior, grounded into the random cation distribution within (but not across) sublattices. In particular, the Zn-containing NFs display complex magnetic structures at low temperature. The substitution of a single cation (20% of the cationic content) changes the FIM-PM *T*<sub>C</sub> by about 130 K. More insight into this fascinating magnetism could be obtained by investigating the details of the cation distribution, as recently carried out for  $(\text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2})_3\text{O}_4$ .<sup>65</sup> Furthermore, the suggested magnetic structure of our HESO NFs should be proved by direct techniques such as neutron diffraction. Of course, the randomness inherent in HEMs makes such detailed investigations a difficult endeavor.

## Author contributions

Conceptualization, A. P. and S. S.; methodology, C. T., B. P., A. M. F., G. P., V. D. N. and X. W.; validation and formal analysis, C. T., A. M. F., G. P. and V. D. N.; data curation, A. P., C. T., A. M. F., G. P., V. D. N. and S. S.; writing—original draft preparation, A. P. and S. S.; writing—review and editing, A. P., N. P. and S. S. All authors have read and agreed to the published version of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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