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# Structure and magnetic phase transitions in $(Ni_{1-x}Co_x)Cr_2O_4$ spinel nanoparticles

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### ARTICLE INFO

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 $NiCr_2O_4$  and  $CoCr_2O_4$  are two distinct members of the chromite family ( $ACr_2O_4$ ) having unique structural and magnetic properties. This paper is a continuation of previous work [Mohanty et al., J. Magn. Magn. Mater. 451(2018)20] and is focused on the modification of ferrimagnetic properties in  $NiCr_2O_4$  by substituting Co ions at Ni sites. In order to do so  $(Ni_{1-x}Co_x)Cr_2O_4$  (x = 0, 0.50, 0.75, 1.00) powder samples were synthesized using chemical co-precipitation techniques. Interest is primarily on (Ni<sub>0.5</sub>Co<sub>0.5</sub>)Cr<sub>2</sub>O<sub>4</sub> and (Ni<sub>0.25</sub>Co<sub>0.75</sub>)Cr<sub>2</sub>O<sub>4</sub> as characterization results on the end members have been reported. It was determined with in-situ temperature dependent X-ray diffraction measurements that these compositions become fully crystallized cubic spinels with space group Fd3m above 700 °C. All samples were subsequently calcined at 900 °C to ensure phase purity and uniform crystallinity. Transmission electron microscopy showed non-uniform distribution of particle sizes with the majority of the particles having bi-pyramidal structures with flat tops for both samples. A comparative account of different ferrimagnetic Curie temperature,  $\theta_f$  or  $T_{C}$ , estimations are presented as determined from measured temperature dependences of the following techniques: Fits of the magnetic susceptibility data indicated a minimum value for the  $(Ni_{0.5}Co_{0.5})Cr_2O_4$  sample at 56.1  $\pm$  0.9 K, followed by an increase to 76.8  $\pm$  0.4 K for the (Ni<sub>0.25</sub>Co<sub>0.75</sub>)Cr<sub>2</sub>O<sub>4</sub> sample; Neutron diffraction measurements gave values of 80  $\pm$  1 K and 87  $\pm$  1 K; Their paramagnetic Curie points,  $\theta_p$ , were determined to be 73.3 and 84.9 K, respectively. The magnetic frustration index  $f = \Theta_{CW}/T_C$  was found to decrease continuously over the series from 11.9 for NiCr<sub>2</sub>O<sub>4</sub> to 7.1 and 6.5 for x = 0.5 and 0.75 respectively with  $(Ni_{0.5}Co_{0.5})Cr_2O_4$  being more frustrated than (Ni<sub>0.25</sub>Co<sub>0.75</sub>)Cr<sub>2</sub>O<sub>4</sub>. Magnetization as a function of applied magnetic field measured at 3 K demonstrates unusually high coercivity for  $(Ni_{0.5}Co_{0.5})Cr_2O_4$ , supporting the notion for the higher degree of magnetic frustration in this sample. No exchange bias was observed for M ( $\mu_0 H$ ) in the (Ni<sub>0.25</sub>Co<sub>0.75</sub>)Cr<sub>2</sub>O<sub>4</sub> sample measured at 3 K, but did however show a significant anomaly in its hysteresis loop at this temperature. The anomaly in hysteresis behaviour disappeared when measured at 1.7 K and also at higher temperatures. Frequency dependent acsusceptibility measurements revealed no shift in the peak position with frequency refuting the existence of spinglass like behavior in both these samples.

# 1. Introduction

NiCr<sub>2</sub>O<sub>4</sub> and CoCr<sub>2</sub>O<sub>4</sub> are ferrimagnetic materials that crystalize into the normal spinel structure having a general formula  $ACr_2O_4$  [1,2], where *A* refers to the tetrahedral site occupied by the magnetic Ni<sup>2+</sup> and Co<sup>2+</sup> ions, whilst the Cr ions are found in the octahedral (*B*) site of the crystal lattice [1]. The interactions between the magnetic cations result in a complex magnetic phase diagram at low temperature [2]. NiCr<sub>2</sub>O<sub>4</sub> and CoCr<sub>2</sub>O<sub>4</sub> both have distinct ferrimagnetic Curie temperatures, *T*<sub>C</sub> = 74 K [1] and 93 K [3], respectively. In the case of NiCr<sub>2</sub>O<sub>4</sub>, a collinear antiferromagnetic component appears below 31 K, whereas in the case of CoCr<sub>2</sub>O<sub>4</sub>, a short-range-ordered (SRO) spiral component evolves that provides a conical magnetic structure below 24 K [4,5]. The conical spin structure contains a uniform and transverse spiral spin state that has an incommensurate propagation vector [*qq*0] with  $q \approx$ 0.63 [5] that lead to ferroelectric properties in CoCr<sub>2</sub>O<sub>4</sub> [3]. A further lock-in-transition appears below 15 K at a slightly smaller *q* value [6].

Structurally, NiCr<sub>2</sub>O<sub>4</sub> crystallizes as cubic spinel with space group Fd3m, shown in Fig. 1 at temperatures above 310 K [7]. At temperatures below 310 K, orbital degeneracy on tetrahedral Ni<sup>2+</sup> leads to

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**Fig. 1.** Crystal structure of a normal cubic spinel with Fd3m space group, obtained using VESTA software [13]. Tetrahedral *A* sites are occupied with divalent cations and octahedral *B* sites are occupied with trivalent cations. Oxygen atoms are shown as red balls at the corners. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

cooperative Jahn-Teller distortion that lowers the structural symmetry from cubic to tetragonal ( $I4_1/amd$ ) with elongated NiO<sub>4</sub> tetrahedra [7]. Further distortion in the tetragonal structure observed in thermodynamic and magnetization measurements [8,9] and leads to an orthorhombic (*Fddd*) phase at 65 K. The  $T_C$  is found to increase above room temperature with Fe substitution at the Cr site indicating the properties follow the characteristics of CoFe<sub>2</sub>O<sub>4</sub> [10]. However, CoCr<sub>2</sub>O<sub>4</sub> displays no such structural phase transition associated with the low temperature magnetic phase transitions [2].

Since Co and Ni have similar ionic radii and oxidation states, it is thus interesting to study the effect that Co substitution at the Ni site has on both the crystal structure and magnetic phase transitions. This is done by experimental measurements of the low temperature magnetic properties of  $(Ni_{1-x}Co_x)Cr_2O_4$  (x = 0, 0.50, 0.75 and 1) along with the a comparative study of the estimation of  $T_C$  values using different approaches.

# 2. Experimental

### 2.1. Sample preparation

 $(Ni_{1-}xCo_x)Cr_2O_4$  (x = 0, 0.50, 0.75 and 1) powders were synthesized by chemical co-precipitation techniques. In this technique stock solutions of 0.5 M of nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O), cobalt nitrate (Co (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) and chromium nitrate (Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) were mixed to the desired amounts in a beaker and stirred continuously for 1 h using a magnetic stirrer to ensure homogeneous mixing. Diluted aqueous ammonia (30%) solution was then added to maintain the *p*H level at 9.8. The precipitates were filtered, then washed several times – firstly with distilled water, followed by acetone and then with ethanol to evaporate the volatile impurities. Finally, the precipitated powders were dried at 100 °C and the conglomerate crushed to a powder. In order to obtain good crystallinity and crystallographic phase purity the samples were calcined at 900 °C for 2 h in a tubular furnace at ambient atmosphere.

# 2.2. Characterization techniques

Structural characterizations of these samples were carried out using a Phillips PAN analytical X-pert Pro X-ray diffractometer (XRD)

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**Fig. 2.** *In-situ* temperature dependent XRD patterns of the (a)  $(Ni_{0.5}Co_{0.5})Cr_2O_4$ , (b)  $(Ni_{0.25}Co_{0.75})Cr_2O_4$  powders synthesized at pH = 9.8 showing the evolution of crystal structure. '\*' denotes the peak associated with the  $Cr_2O_3$  impurity phase.

utilizing Cu-K $\alpha$  radiation ( $\lambda = 1.54056$  Å). Temperature dependent XRD studies were carried out in-situ in a non-ambient Anton Parr HTK 1200 Oven-Chamber attachment capable of temperatures from room temperature to 1200 °C under He or air atmospheres. Data were acquired in a 20 range of  $10^{\circ} \le 2\theta \le 80^{\circ}$ , with a hold time of 10 min before each measurement carried out under He atmosphere. The instrument is equipped with an incident beam hybrid monochromator that delivers a quasi-parallel X-ray beam to minimize effects associated with possible sample height deviations during the course of heating. A JEM-2100 transmission electron microscope (TEM) was employed to investigate the microstructure of the calcined powders. Magnetic measurements were performed using a 14T Cryogen Free Physical and Magnetic Measurement System (CRYOGENIC Ltd., UK) with a vibrating sample magnetometer (VSM) insert [11], under zero-field cooled (ZFC) and field cooled (FC) protocols. In the ZFC protocol, the sample was initially cooled to 2 K where the probing field was applied and the measurements commenced during the heating cycle. In the FC protocol, the sample was cooled to 2 K in an applied probing magnetic field and measurements performed during heating the sample in this field. Temperature dependent neutron diffraction measurements were carried



**Fig. 3.** Rietveld refinement of XRD patterns of the (a) (Ni<sub>0.5</sub>Co<sub>0.5</sub>)Cr<sub>2</sub>O<sub>4</sub> and (b) (Ni<sub>0.25</sub>Co<sub>0.75</sub>)Cr<sub>2</sub>O<sub>4</sub> and (c) CoCr<sub>2</sub>O<sub>4</sub> powders synthesized at *p*H ~ 9.8 and calcined at 900 °C for 3 h. Measured data are indicated with the open symbols with Rietveld refinements indicated with red solid lines. The plots in blue show the difference curves between measured and refined data. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

out on the PITSI instrument at a wavelength of 1.76 Å and equipped with a closed cycle cryogenic system, at Necsa, South Africa [12].

# 3. Results and discussion

Fig. 1 shows the crystal structure of a normal cubic spinel as generated using the VESTA software [13]. In order to study the phase formation during calcination, in-situ high temperature powder XRD measurements were performed on the  $(Ni_{1-x}Co_x)Cr_2O_4$  (x = 0.50, 0.75) samples for temperatures between 35 and 1100 °C (Fig. 2). At 35 °C no distinct peaks are observed indicating the amorphous nature of the starting phases. With increased temperature, crystalline phase formation develops at 500 °C as observed by the appearance of diffraction peaks corresponding to the major (2 2 0), (3 1 1), (4 0 0), (5 1 1) and (4 4 0) reflections of the  $(Ni_{1-x}Co_x)Cr_2O_4$  phase [4]. The broadness of the peaks is attributed to the size of the particles [14]. Also, the appearance of the  $Cr_2O_3$  phase, indicated with an asterisk (\*) in Fig. 2, is observed in both samples as an intermediate phase. Upon further heating to 700 °C, the Cr<sub>2</sub>O<sub>3</sub> phase disappeared and the structure remained cubic up to the highest measurement temperature of 1100 °C. Thus, considering this data confirming the phase formation temperature, it was decided to calcine the samples at 900 °C to avoid the presence of any Cr<sub>2</sub>O<sub>3</sub> phase and to retain the nanometric crystallite size.

The preliminary results for these samples were reported in Ref. 15 and compared with both the end products  $\text{CoCr}_2\text{O}_4$  and  $\text{NiCr}_2\text{O}_4$ . Co and Ni were found to be in 2+ and Cr in 3+ oxidation states, as confirmed by X-ray photoelectron spectroscopy. Variations of the coercivity ( $H_c$ ), remanent magnetization ( $M_R$ ), saturation magnetization ( $M_s$ ) with compositions x = 0.5 and 0.75 indicated  $T_c$  values 89.2  $\pm$  0.7 K and 90.6  $\pm$  0.9 K at a probing field of 0.5 T respectively using a knee-point method. Unusually high coercivity of 3.6  $\pm$  0.7 T was observed for the x = 0.5 sample.

The present work reports on additional M(T) measurements carried out with different probing fields to obtain deeper insight into the magnetic properties and theoretical simulation of the magnetic frustration. To understand the anomalous kink in  $M(\mu_0H)$  data observed at 3 K, additional measurements were performed using different cooling fields and temperatures. Possible spin-glass like behaviour was probed utilizing frequency dependent ac-susceptibility measurements. Furthermore, low temperature neutron diffraction measurements were carried out to unambiguously locate the  $T_{\rm C}$ 's.

Fig. 3 (a) and (b) show XRD data at 300 K, as well as Rietveld refinement simulations for the  $(Ni_{1-x}Co_x)Cr_2O_4$ , x = 0.50, 0.75, samples calcined at 900 °C. For comparison, result from the CoCr<sub>2</sub>O<sub>4</sub> sample is shown in Fig. 3 (c). The structural parameters obtained from the Rietveld refinement process are given in Table 1. This indicates that all three samples crystallize in the Fd3m cubic phase in contrast to the known tetragonal phase of NiCr<sub>2</sub>O<sub>4</sub> [15] at 300 K. It is obvious that the substitution of Ni by Co on the Ni site stabilizes the formation of the cubic structure [15]. This in addition leads to an expansion in the lattice parameters from 8.322 Å to 8.326 Å for x = 0.5 to x = 0.75 Co, respectively, that is attributed to the larger ionic radius of Co compared to the Ni ion [15]. On the diffraction patterns of Fig. 3 this is observed by slight shifts in the Bragg peak positions towards lower 20 values, as was reported earlier [15]. It is known that stress in bulk samples also influences the peak positions, but such macro stresses cannot be sustained in powders and thus not a contributing factor. The average crystallite size determined using Scherer's formula is about 45(2) nm for x = 0.5and about 50 (1) nm for x = 0.75.

In Fig. 4 TEM micrographs of  $(Ni_{1-x}Co_x)Cr_2O_4$ , with x = 0.50 (a) and 0.75 (b) samples calcined at 900 °C, are given. It is clear that both the samples have non-uniform particle shapes and sizes. Particle size histogram analyses shown in Fig. 5 indicate that the average particle size initially increase from 72  $\pm$  5 nm for the x = 0 sample, to a maximum of 115  $\pm$  4 nm for x = 0.5, where after it decreased to

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#### Table 1

Structural parameters obtained from Reitveld refinement of (Ni<sub>0.5</sub>Co<sub>0.5</sub>)Cr<sub>2</sub>O<sub>4</sub>, (Ni<sub>0.25</sub>Co<sub>0.75</sub>)Cr<sub>2</sub>O<sub>4</sub> and CoCr<sub>2</sub>O<sub>4</sub>.

Refined Parameters (Structure Cubic, Space Group: $Fd3m$ )	$(Ni_{0.5}Co_{0.5})Cr_2O_4$	$(Ni_{0.25}Co_{0.75})Cr_2O_4$	CoCr <sub>2</sub> O <sub>4</sub>
a, b, c [Å]	8.322	8.326	8.326
$\chi^2$	1.08	1.76	1.39
Bragg R-factor	1.75	1.83	2.65
<i>RF</i> -factor	2.49	2.52	3.92
Ni (x, y, z)	(0.125, 0.125, 0.125)	(0.125, 0.125, 0.125)	-
Co ( <i>x</i> , <i>y</i> , <i>z</i> )	(0.125, 0.125, 0.125)	(0.125, 0.125, 0.125)	(0.125, 0.125, 0.125)
$\operatorname{Cr}(x, y, z)$	(0.5, 0.5, 0.5)	(0.5, 0.5, 0.5)	(0.5,0.5,0.5)
O ( <i>x</i> , <i>y</i> , <i>z</i> )	(0.26, 0.26, 0.26)	(0.26035, 0.26035, 0.26035)	(0.25979, 0.25979, 0.25979)



**Fig. 4.** Transmission electron microscopy (TEM) images of (a)  $(Ni_{0.5}Co_{0.5})Cr_2O_4$  and (b)  $(Ni_{0.25}Co_{0.75})Cr_2O_4$  (Insets show the enlarged view of a single particle). High resolution electron microscopy images of (c)  $(Ni_{0.5}Co_{0.5})Cr_2O_4$  and (d)  $(Ni_{0.25}Co_{0.75})Cr_2O_4$  (Insets show the selected area electron diffraction (SAED) patterns). Note: Relevant scales are given by the bar lengths).

91  $\pm$  4 nm for x = 0.75, and 52  $\pm$  1 nm for x = 1. The average particle sizes are in line with the values obtained by taking the mean diameter of the particles [15]. These values are larger than the average crystallite sizes calculated from the XRD, indicating polycrystalline nature of the particles [16]. The insets of Fig. 4 (a) and (b) show zoomed TEM views of isolated particles for each composition, indicating similar morphologies and bi-pyramidal shapes with the tips of the bi-pyramid being flat rather than sharp. This was previously reported in NiCr<sub>2</sub>O<sub>4</sub>, as a characteristic structure for spinel compounds [17] and is maintained on substituting Ni with Co in the lattice. The highly crystalline nature of the  $(Ni_{0.5}Co_{0.5})Cr_{2}O_{4}$ and (Ni<sub>0.25</sub>Co<sub>0.75</sub>)Cr<sub>2</sub>O<sub>4</sub> particles is demonstrated by the distinct lattice fringes observed in the high resolution transmission electron microscopy (HRTEM) images shown in Fig. 4 (c) and (d), respectively. The spotty ring patterns related to the (4 4 0), (4 4 4) and (6 4 2) planes observed from the selected area electron diffraction (SAED: Insets) images confirm the high level of crystallinity of the nanoparticles, in correlation with the XRD results (Fig. 3) and the parameters shown in Table 1. Determination of the *d*-spacing related to the (1 1 1) plane from the lattice fringes gives 5.39 Å for x = 0.5 and 5. 53 Å for x = 0.75 which are larger than the expected values. This may be related to a possible lattice expansion observed in nanoparticles [18].

The temperature dependence of the magnetization, M(T), and applied magnetic field,  $M(\mu_0 H)$ , were carried out in zero field cooled  $(M_{\rm ZFC})$  and field cooled  $(M_{\rm ZFC})$  conditions by applying probing magnetic fields of magnitudes 0.1, 0.5, 1 and 2 T, respectively. M(T) data using only 0.5 T probing field were previously reported [15]. M<sub>ZFC</sub> and M<sub>FC</sub> investigations were done as described in the experimental section. After each measurement run of zero-field cooled (ZFC) and field cooled (FC) experiments, the samples were heated to 300 K to ensure that the sample regained the paramagnetic phase. Results are shown in Fig. 6 (a) and (b) for (Ni<sub>0.5</sub>Co<sub>0.5</sub>)Cr<sub>2</sub>O<sub>4</sub> and (Ni<sub>0.25</sub>Co<sub>0.75</sub>)Cr<sub>2</sub>O<sub>4</sub> samples, respectively, for the different probing magnetic fields indicated. In all measurements  $M_{\rm FC}(T)$  does not follow the  $M_{\rm ZFC}(T)$ , indicating prominent irreversibility at low temperatures. This is due to the magnetic frustration typically observed in these chromite systems [19,20] as discussed in the next paragraphs.  $M_{ZFC}(T)$  curves show a hump at low temperatures for the  $(Ni_{0.5}Co_{0.5})Cr_2O_4$  sample (Fig. 6 (a)), whereas  $M_{\rm FC}(T)$  shows significant broadening of the hump and its expansion at low temperatures. In the case of the (Ni<sub>0.25</sub>Co<sub>0.75</sub>)Cr<sub>2</sub>O<sub>4</sub> sample, the



Fig. 5. Particle size histograms obtained from the TEM images for (a) NiCr<sub>2</sub>O<sub>4</sub>, (b) (Ni<sub>0.5</sub>Co<sub>0.5</sub>)Cr<sub>2</sub>O<sub>4</sub>, (c) (Ni<sub>0.25</sub>Co<sub>0.75</sub>)Cr<sub>2</sub>O<sub>4</sub> and (d) CoCr<sub>2</sub>O<sub>4</sub>. X<sub>C</sub> represents the average particle sizes.

hump in magnetization is significant in both the  $M_{\rm ZFC}(T)$  and  $M_{\rm FC}(T)$ curves (Fig. 6 (b)). The  $M_{FC}(T)$  behaviour also shows an increase in the value of the magnetization at low temperatures (Fig. 6 (b)). For both the samples, the slopes near  $T_{\rm C}$  in  $M_{\rm ZFC}(T)$  and  $M_{\rm FC}(T)$  increases towards higher temperature with increasing probing field strength. Similar shifting of slopes towards higher temperature with increasing field was also reported previously for the case of Fe doped CoCr<sub>2</sub>O<sub>4</sub> [20]. The bifurcation in  $M_{ZFC}(T)$  and  $M_{FC}(T)$  curves, represented by the difference in these curves, is higher for the 2 T field in the (Ni<sub>0.5</sub>Co<sub>0.5</sub>)Cr<sub>2</sub>O<sub>4</sub> sample when compared with the (Ni<sub>0.25</sub>Co<sub>0.75</sub>)Cr<sub>2</sub>O<sub>4</sub> sample, suggesting an increase in the frustration in the former [19,20]. Further, considering the ZFC data, dM/dT as a function of temperature plots are shown in Fig. 7 to facilitate in the determination of the magnetic transitions. For the  $(Ni_{0.5}Co_{0.5})Cr_2O_4$  sample two transitions, labeled as T1 and T2 corresponding to temperatures 20 and 32 K, respectively below  $T_C$  (Fig. 7 (a)) are observed which become more prominent with increased field. Here T<sub>2</sub> possibly corresponds to the ordering of the antiferromagnetic component as seen in NiCr<sub>2</sub>O<sub>4</sub> [4]. However, the origin of the transition at 20 K related to  $T_1$  is not clear. Retention of bifurcation in  $M_{ZFC}(T)$  and  $M_{FC}(T)$  up to a 2 T applied field at low temperatures seen in Fig. 6 is usually associated with the

frustrated nature of the nanoparticles [19]. To demonstrate thispoint,  $\Delta M = |M_{\rm ZFC} - M_{\rm FC}|$  as a function of temperature plots are shown in Fig. 8 for the x = 0.5 and x = 0.75 samples at the different probing magnetic fields. Overall,  $\Delta M$  decreases with increasing probing field up to 2 T, except for the x = 0.5 sample where the difference at low temperature exceeds that measured at 0.1 T (Fig. 8 (a) and (b)). For the x = 0.75 sample (Fig. 6 (b)) the spiral ordering and lock-in-transitions, at temperatures of approximately 26 K and 6.5 K, respectively, become more prominent compared to the x = 0.5 sample (Fig. 6 (a)). The  $M_{\rm ZFC}(T)$  for (Ni<sub>0.25</sub>Co<sub>0.75</sub>)Cr<sub>2</sub>O<sub>4</sub> shows negative magnetization values when measured under a probing field of 0.5 T (Fig. 6 (b)). This type of behaviour in ferrimagnets is often ascribed to the change in the direction of the magnetization in the ferromagnetic component at the compensation temperature [15,21,22]. In the case of spinel compounds having A and B sublattices with different magnetizations associated with their crystallographic sites, the resultant magnetization changes sign at a temperature known as the compensation temperature [21,22]. The negative magnetization in these systems mostly arises due to the presence of uncompensated spins [22–24]. The dM/dT for the NiCr<sub>2</sub>O<sub>4</sub> and  $CoCr_2O_4$  samples are shown in Fig. 7 (c) with the characteristic transitions labeled.

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Fig. 6. Temperature-dependent magnetization under zero field cooled (ZFC) and field cooled (FC) protocols for the (a)  $(Ni_{0.5}Co_{0.5})Cr_2O_4$  and (b)  $(Ni_{0.25}Co_{0.75})Cr_2O_4$  samples with different probing fields.

For a standard ferrimagnetic material, the theoretical variation of reciprocal susceptibility with temperature in the paramagnetic region is expressed as [25]:

$$\chi^{-1} = \frac{T}{C} + \frac{1}{\chi_0} - \frac{b}{T - \theta}$$
(1)

where *T* is the temperature, *C* is the Curie constant, *b*,  $\theta$  and  $\frac{1}{\chi_0}$  are constants. The above equation represents a hyperbola containing a Curie-Weiss (ferrimagnetic) term and a Curie (paramagnetic) term [25]. The significance of the paramagnetic term is associated with the non-saturation behaviour as demonstrated by certain chromites [20]. As the studied materials are ferrimagnetic, equation (1) is used to fit the reciprocal susceptibility as a function of temperature, as shown in Fig. 9. The high temperature (paramagnetic) experimental data is well fit with the equation with a deviation occurring near the Curie temperature. Similar results have previously been reported where there is discrepancy between experimental and theoretical fitting results [25]. The fitting parameters are summarized in Table 2. By linear extrapolation of the experimental data points below this Curie temperature to zero susceptibility, the intercept with the temperature axis gives the temperature  $\theta_f$  (or  $T_C$ ) called the ferrimagnetic Curie point ( $T_C$ ) [25]. The

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**Fig.7.** dM/dT as a function of temperature measured under ZFC conditions for (a) (Ni<sub>0.5</sub>Co<sub>0.5</sub>)Cr<sub>2</sub>O<sub>4</sub>, (b) (Ni<sub>0.25</sub>Co<sub>0.75</sub>)Cr<sub>2</sub>O<sub>4</sub>, and (c) NiCr<sub>2</sub>O<sub>4</sub> and CoCr<sub>2</sub>O<sub>4</sub>. Legends depict the probing fields.

susceptibility diverges at temperatures lower than this point due to the appearance of spontaneous magnetization. The values of  $\theta_f$  for  $(Ni_{0.5}Co_{0.5})Cr_2O_4$  and  $(Ni_{0.25}Co_{0.75})Cr_2O_4$  are 56.2  $\pm$  0.9 K and 76.8  $\pm$  0.4 K respectively. The data fitted with equation (1) intersects



Fig. 8.  $\Delta M = |M_{FC} - M_{ZFC}|$  plots as a function of temperature for (a) (Ni<sub>0.5</sub>Co<sub>0.5</sub>)Cr<sub>2</sub>O<sub>4</sub> and (b) (Ni<sub>0.25</sub>Co<sub>0.75</sub>)Cr<sub>2</sub>O<sub>4</sub>.

the temperature axis at  $\theta_p$ , which is called the paramagnetic Curie point. The values of  $\theta_p$  found for (Ni<sub>0.5</sub>Co<sub>0.5</sub>)Cr<sub>2</sub>O<sub>4</sub> and (Ni<sub>0.25</sub>Co<sub>0.75</sub>)  $Cr_2O_4$  are 73.3 and 84.9 K, respectively, (Fig. 9). The appearance of two Curie temperatures which are not identical, termed as  $\theta_p$  and  $\theta_f$ , respectively representing paramagnetic and ferrimagnetic Curie temperatures is commonly observed in ferrimagnetic compounds [25]. The temperature difference between  $\theta_p$  and  $\theta_f$  indicates that the ferrimagnetic to paramagnetic phase transition is not strongly defined, but smeared out, which is in line with the reported results for ferrimagnets [25]. The smeared or diffused nature, of the transition is due to the presence of spin clusters in the material [25]. These spin clusters are small group of atoms having parallel spins over a small temperature regime above  $\theta_n$ , giving rise to a short-range order. This temporal spin order disappears with increasing temperature above  $\theta_p$ . Below  $\theta_f$  a long range order of spin persists even in the absence of external magnetic field [25]. A careful analysis of the fits, as shown in Fig. 9, indicates that the data for (Ni<sub>0.25</sub>Co<sub>0.75</sub>)Cr<sub>2</sub>O<sub>4</sub> fits well to the equation when compared to that of the other sample. It affirms the previous notion that the (Ni<sub>0.5</sub>Co<sub>0.5</sub>)Cr<sub>2</sub>O<sub>4</sub> is magnetically more frustrated at low temperatures, which subsequently leads to the deviation from the expected theoretical values [26]. At high temperatures the last term of equation (1) becomes negligible and the equation reduces to a Curie-Weiss law [26]:

$$\chi = \frac{C}{T + (C/\chi_0)} \tag{2}$$

where *C* is the Curie constant, *T* is the temperature and  $\chi_0$  is a constant [25]. Equation (2) represents a straight line, to which  $(1/\chi)$  as function of *T* curves becomes asymptotic at high temperatures. There is a disagreement between theoretical and experimental values for  $T_{\rm C}$  and this is due to the short-range spin order (in the spin clusters) at temperature  $\theta_{\rm f}$  [27]. The fitting parameters using equation (1) and the estimated values of the frustration index  $f = \theta_{\rm CW}/T_{\rm C}$  are calculated and listed in Table 2 [28]. The frustration parameter *f* is highest for the NiCr<sub>2</sub>O<sub>4</sub> and decreases with Co substitution at the Ni site from 7.1 to 6.5 with increasing *x* from 0.5 to 0.75, indicating that the Co addition stabilized the structure, with CoCr<sub>2</sub>O<sub>4</sub> having the least frustration index *f*. The large value of *f* for NiCr<sub>2</sub>O<sub>4</sub> possibly implies the occurrence of structural changes at the onset of the magnetic transitions.

It has been reported that for CoCr<sub>2</sub>O<sub>4</sub> nanoparticles with average size ranging from 8 to 10 nm, the  $T_{\rm C}$  remains unaffected by reducing the particle size to nano-scale range, or having a non-uniform distribution of particles [19]. However, in similar spinel structures such as MnFe<sub>2</sub>O<sub>4</sub> nanoparticle ferrites, a significant increase in T<sub>C</sub> has been reported compared to the bulk value when the particle size is reduced to nanoscale range (7.5-24.5 nm) [29,30]. The shift in Curie temperature was described by a finite size scaling formula  $[T_C(d) - T_C(\infty)]/T_C(\infty) = (d/d)$  $d_0$ )<sup>-1/ $\nu$ </sup> [31]. Here, d is the size of the nanoparticles,  $T_{\rm C}(\infty)$  is the  $T_{\rm C}$ related to the bulk value,  $d_0 = 2.0$  nm and  $\nu = 0.71 \pm 0.071$  [31]. However, the present work does not allow for the estimation of the exponent values since the size dependence of  $T_{\rm C}$  is not known for the material [32]. It is further noted that two different compositions having different particle sizes are not comparable. In addition, an important aspect to take note of is the average particle size. The scaling law is valid for the sizes ranging from 7.5 to 24.4 nm in the case of MnFe<sub>2</sub>O<sub>4</sub> [31]. However, in our case, the average particle size ranges from 50 to 102 nm. In the case of CoCr<sub>2</sub>O<sub>4</sub> nanoparticels particle size had no dependence on  $T_{\rm C}$  [19,32]. On the other hand Dutta et al. [22] reported the reduction of  $T_{\rm C}$  from 98 to 84 K when the particles were reduced to nanoscale (30-40 nm), contradicting the scaling feature reported by Tanng et al. [31]. From the above findings it can be concluded that the  $T_{\rm C}$  of these nanoparticles are evidently dependent on the particle size, but the relation is difficult to predict.

In order to investigate the magnetic behaviour further, magnetization, *M*, as a function of applied magnetic field,  $B = \mu_0 H$ , measurements were done at different constant temperatures for both ZFC and FC conditions. The results of these studies are shown in Fig. 10 and Fig. 11. The  $M(\mu_0 H)$  loop for (Ni<sub>0.5</sub>Co<sub>0.5</sub>)Cr<sub>2</sub>O<sub>4</sub> shifts towards larger negative values when measured under FC conditions with fields of 0.1 T and 0.5 T (Fig. 10 (a)), indicating the presence of exchange bias effects in the system. The coercivity is found to be 3.6 T for the  $(Ni_{0.5}Co_{0.5})Cr_2O_4$ sample, which is higher compared to the conventional ferrimagnetic materials [25]. In addition careful observation of the magnetization indicated an anomalous change in the slope of the curve at about 5 T. For clarity, a zoomed view is shown as Fig. 10 (b) within the low field region. In the positive quadrant the behaviour of the magnetization for the sample's hysteresis loops measured at 3 K is found to be mostly independent of the cooling field, but on the negative quadrant the magnetization values shifts more when the sample is cooled under 0.5 T field than compared to cooling in a 0.1 T field (Fig. 10 (b)). Upon increasing the temperature to 56 K the exchange bias effect disappears (Fig. 10 (c)). For both the measurements taken at 3 K and 56 K, the magnetization is not saturated in an applied field of 12 T. Hence, the true nature of the observed exchange bias is disputed [15]. The fact that the  $M(\mu_0 H)$  does not saturate is an indication of the non-collinear magnetic structure of these compounds and similar results have been



Fig. 9. Reciprocal susceptibility as a function of temperature for (a) Ni $Cr_2O_4$ , (b) (Ni $_{0.5}Co_{0.5}$ ) $Cr_2O_4$ , (c) (Ni $_{0.25}Co_{0.75}$ ) $Cr_2O_4$  and (d) Co $Cr_2O_4$  measured under a probing field of 0.5 T. The solid line in the figure refers to equation (1) given in the text.

Table 2 Results from the fitting the inverse magnetic susceptibility data to the Curie-Weiss equation for the Ni <sub>1-x</sub> Co <sub>x</sub> Cr <sub>2</sub> O <sub>4</sub> samples.									
$Ni_{1-x}Co_xCr_2O_4 \ (x = 0, \ 0.50, \ 0.75, \ 1)$	Fitting Parameters			$\Theta_{CW}$	$\theta_p$	$\theta_f$ or $T_C$	$f = \Theta_{\rm CW}/T$		
	$1/\chi_0$	b	θ	С					
x = 0	167	2120	55	69	-786 K	67.5 K	65.6 ± 0.5 K	11.9	
x = 0.50	140	2540	55	75	- 399 K	73.3 K	56.1 ± 0.9 K	7.1	
x = 0.75	160	4180	59	80	-502 K	84.9 K	$76.8 \pm 0.4 \text{ K}$	6.5	
x = 1	175	4800	68	105	-520 K	95.6 K	93.7 ± 0.5 K	5.5	

reported in Mn doped CoCr<sub>2</sub>O<sub>4</sub> [28]. It was suggested [33] that the linear increase in magnetization was the result of the distortion of the lattice during the structural transition and suppression of ferromagnetic interactions induced by Mn ions that created an increased frustration in the system [33]. Though, in MnCr<sub>2</sub>S<sub>4</sub> single crystals similar behaviour is regarded as the coexistence of a ferrimagnetic and quasi-paramagnetic contribution arising only because of the nonlinear spin structure of *B* site Cr<sup>3+</sup> ions [34]. For the (Ni<sub>0.25</sub>Co<sub>0.75</sub>)Cr<sub>2</sub>O<sub>4</sub> sample, the  $M(\mu_0H)$  loop measured at 1.7 K does not show a kink (Fig. 11 (a)). The coercivity is found to be 2.2 T. However, the hysteresis loop measured at 3 K shows an anomaly similar to the (Ni<sub>0.5</sub>Co<sub>0.5</sub>)Cr<sub>2</sub>O<sub>4</sub> sample at an applied magnetic field of about 2.3 T (Fig. 11 (c): zoomed in view of Fig. 11 (b)) both measured under ZFC and FC protocols. The anomaly suggests the moments comprise of soft and hard magnetic components where the

soft component does not couple strongly to the hard-magnetic component to cause a change in slope in the hysteresis loop [35]. Similar kinks in the hysteresis loop are mostly observed in multilayered thin films due to exchange-decoupling [36]. The hysteresis loop measured at a cooling field of 0.5 T almost mimics the ZFC curve (Fig. 11 (c)). Similar anomalies in  $M(\mu_0H)$  plots were observed for manganite bilayers of collinear ferromagnetic La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>4</sub> and non-collinear multiferroic TbMnO<sub>3</sub> [34]. In that case the pronounced exchange bias and the enhancement of coercivity in the bilayer was because of the existence of strong interfacial exchange coupling which is a consequence of the presence of uncompensated spins at the interface between the antiferromagnetic TbMnO<sub>3</sub> and ferromagnetic La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>4</sub> [37]. In the present case the surface spins at the grain boundaries almost act like different layers and the modification in the sub-lattice magnetization



**Fig. 10.** Magnetic field dependent magnetization measurement,  $M(\mu_0 H)$ , for (Ni<sub>0.5</sub>Co<sub>0.5</sub>)Cr<sub>2</sub>O<sub>4</sub> sample measured under zero field cooled (ZFC) and field cooled (FC) protocols at (a) 3 K, (b) 3 K (zoomed in view) and (c) 56 K.

because of cationic substitution leads to an exchange bias as well as a kink in the temperature dependent  $M(\mu_0 H)$  loop. However, this behaviour is only observed at 3 K and not in  $M(\mu_0 H)$  measured at temperatures higher than 20 K, 40 and 70 K for (Ni<sub>0.25</sub>Co<sub>0.75</sub>)Cr<sub>2</sub>O<sub>4</sub> sample (Fig. 11 (d-e)) where no exchange bias is observed. The true nature of exchange-bias in these systems is hard to claim because of the unsaturated hysteresis loops, even seen up to a field of 12 T [15].

Neutron diffraction measurements were done to directly observe the magnetic ordering for the determination of the phase transition and lock-in temperatures, as well as the crystallographic structures at low temperatures. In NiCr<sub>2</sub>O<sub>4</sub> magnetic transitions are associated with structural transitions [7]. The magnetic order is composed of a ferromagnetic component with a transition temperature of 74 K that manifests at the (1 1 1) fundamental reflection, with the manifestation of superlattice reflections below 31 K that are associated with antiferromagnetic ordering observed as peaks at the (1 1 0) and (2 0 1) positions [1]. This transition is related to additional lattice distortion in the same space group that was confirmed with high-resolution synchrotron based XRD measurements that obtained T = 30 K [7]. It was found [5] that the magnetism in CoCr<sub>2</sub>O<sub>4</sub> single crystals orders as a combined ferrimagnetic spiral below  $T_{\rm C} = 93$  K with the magnetic peak manifesting at the (1 1 1) nuclear position. The presence of the ferromagnetic component for all temperatures below  $T_{\rm C}$  implies that it has long-range order whilst the spiral component exhibits short-range order (no major coherent magnetic contribution). The latter component though transforms into long-range incommensurate order with propagation vector (0.63, 0.63, 0) below approximately 24 K that was observed as satellite reflections to (2 2 0) and (2 0 0). With further cooling this magnetic order becomes commensurate below 15 K with a propagation vector of (0.675, 0.675, 0) [38]. The stability of the cubic phase of CoCr<sub>2</sub>O<sub>4</sub> has been confirmed down to 11 K [7].

In Fig. 12, the results of the neutron diffraction measurements down to about 4.2 K are shown for all the samples used in this study. These figures show only the region where the dominant magnetic reflections were observed using a wavelength of 1.76 Å. Fig. 12(a) summarizes the temperature dependence of the diffraction patterns of NiCr<sub>2</sub>O<sub>4</sub> with the magnetic contributions associated with ferromagnetic ordering being superimposed on the (1 1 1) nuclear reflection. The structural (2 2 0) peak observed at 300 K systematically converts into (2 0 2) with decreasing temperature, indicating a structural change. The results are in qualitative agreement with [1]. No evidence of the lower temperature transition is though observed. The other graphs of Fig. 12 indicate that with Co substitution the tetragonal crystal structure converts to an *Fd*3*m* cubic structure for  $x \ge 0.5$ . The ferromagnetic features are observed superimposed on the (1 1 1) nuclear reflection. In order to estimate the  $T_{\rm C}$  values, the integrated intensities of the (1 1 1) peak as a function of temperature are shown in Fig. 13 for all the samples. The magnetization results were analyzed and correlated using the integrated intensities from the temperature dependent neutron diffraction results for the (Ni<sub>0.5</sub>Co<sub>0.5</sub>)Cr<sub>2</sub>O<sub>4</sub> and (Ni<sub>0.25</sub>Co<sub>0.75</sub>)Cr<sub>2</sub>O<sub>4</sub> samples of  $80 \pm 1$  K and  $87 \pm 1$  K, respectively [Fig. 13].

Ferrimagnetic Curie temperature  $T_{\rm C}$ , spiral ordering temperature  $T_{\rm S}$ and lock-in transition  $T_{\rm L}$  were determined from the magnetization measurements [Fig. 6 (b)] for (Ni<sub>0.25</sub>Co<sub>0.75</sub>)Cr<sub>2</sub>O<sub>4</sub> samples using different probing fields. Temperature dependence plots of the neutron diffraction intensities related to the (1 1 1) peaks, [Fig. 13 (c)] show anomalous behaviours below 30 K with Co addition which are attributed to  $T_{\rm S}$ . This anomaly is most prominent in CoCr<sub>2</sub>O<sub>4</sub>. In addition careful observation of the (2 0 1) satellite peak, shown in Fig. 12 (c) for sample (Ni<sub>0.25</sub>Co<sub>0.75</sub>)Cr<sub>2</sub>O<sub>4</sub>, starts to manifest below 24 K. This also supports the claim for the  $T_{\rm S}$ . The (2 0 1) satellite intensities become more prominent with Co content and is most prevalent in the CoCr<sub>2</sub>O<sub>4</sub> compound, corroborating the transition related to  $T_{\rm S}$  [Fig. 12 (d)]. The



**Fig. 11.** Magnetic field dependent magnetization measurements,  $M(\mu_0H)$ , for (Ni<sub>0.25</sub>Co<sub>0.75</sub>)Cr<sub>2</sub>O<sub>4</sub> sample measured under zero field cooled (ZFC) and field cooled (FC) protocols at (a) 1.7 K and (b) 3 K, (c) 3 K (zoomed in view), (d) 20 K and (e) 40 K. Inset on latter shows the ZFC and FC magnetization at 70 K.

appearance of  $T_{\rm S}$  critically depends on the average particle size since Ptak et al. [32] observed the incommensurate spiral magnetic structure below  $T_{\rm S} = 24$  K in particles with mean size of 23 nm, whereas the  $T_{\rm S}$  was not prominent for the particles with average size 4.5 nm. Rath et al. [19] observed  $T_{\rm S} = 23$  K for the nanoparticles with average size

ranging from 8 to 12 nm. Dutta et al. [22] reported  $T_{\rm S} = 25$  K for nanoparticles with size ranging from 30 to 40 nm claiming that the wavelength of the incommensurate magnetic structure is at least ten times that of the chemical unit cell that would be longer than ~10 nm for the CoCr<sub>2</sub>O<sub>4</sub>. Below this size, spiral ordering would not be possible.



Fig. 12. Neutron diffraction patterns as function at fixed temperatures for the samples (a)  $NiCr_2O_4$ , (b)  $(Ni_{0.5}Co_{0.5})Cr_2O_4$ , (c)  $(Ni_{0.25}Co_{0.75})Cr_2O_4$  and (d)  $CoCr_2O_4$  within a selected  $2\theta$  range.

Hence, in the present case the transitions are evident both from the M (T) and the temperature dependent neutron diffraction measurements. The anomalies related to  $T_{\rm S}$  are indicated in the Fig. 13. A zoomed view for the Fig. 13 (b) and (c) are shown as insets for clarity. Superlattice peaks associated with the spiral component manifest at the (2 2 0)-satellite position for temperatures lower than 25 K and becomes more prominent with increased Co substitution [5,38,39] suggesting the onset of a larger magnetic moment as shown in Fig. 12.

The  $T_{\rm C}$  values obtained by the M(T) (using knee-point method) measurements [15], dM/dT, estimation of  $\theta_f$  using equation (1), and neutron diffraction results are collectively listed in Table 3. It is clear that the estimated  $T_{\rm C}$  values for M(T) data using the knee-point method overestimated the temperatures. The data obtained by neutron diffractions are most acceptable as there is no external perturbing parameter influence, such as magnetic field.

In order to understand the spin-dynamics of the system, frequency dependent ac-susceptibility measurements were performed for the  $(Ni_{0.5}Co_{0.5})Cr_2O_4$  and  $(Ni_{0.25}Co_{0.75})Cr_2O_4$  samples as shown in Fig. 14. The real part of the ac-susceptibility showed a cusp for both the samples with significant dispersion with frequency, suggesting magnetic frustration in the system as predicted [35]. For spin-glass systems the peak of the ac-susceptibility shifts to lower temperature with an increase in frequency [40]. In the current study the peak of the ac-susceptibility did not shift with increased frequency (Fig. 10).

However, for  $(Ni_{0.5}Co_{0.5})Cr_2O_4$  the peak splits into a doublet with increasing frequency, whereas the peak for  $(Ni_{0.25}Co_{0.75})Cr_2O_4$  is sharp compared to the previous (Fig. 14 (b)). The broader peak shape of  $(Ni_{0.5}Co_{0.5})Cr_2O_4$  suggests a higher degree of frustration for this sample, as calculated from the frustration index. Magnetization measurements of  $CoCr_2O_4$  nanoparticles with sizes ranging from 8 to 12 nm at a probing magnetic field of 10 Oe revealed that the  $T_s$  was absent [19]. However, an anomaly related to  $T_s$  appeared when M(T) was measured with an increased probing field of 500 Oe [19]. In acsusceptibility measurements with different frequencies and probing field of 3 Oe the  $T_s$  feature was absent in the real part of the ac-susceptibility [19]. From this it can be inferred that the transition related to  $T_s$  is sensitive to the probing field.

### 4. Conclusions

 $(Ni_{0.5}Co_{0.5})Cr_2O_4$  and  $(Ni_{0.25}Co_{0.75})Cr_2O_4$  powder samples were synthesized using chemical co-precipitation techniques. The as-synthesized samples were amorphous in nature. From *in-situ* temperature dependent XRD measurements it was observed that the cubic phase had fully crystalized around 700 °C with no further change in crystallographic structure observed upon heating to 1100 °C. Samples calcined at 900 °C were subsequently used for microstructural and magnetic studies. TEM analyses showed non-uniform particle size distribution with



**Fig. 13.** Integrated neutron intensities of (1 1 1) peak as a function of temperature for (a) NiCr<sub>2</sub>O<sub>4</sub>, (b) (Ni<sub>0.5</sub>Co<sub>0.5</sub>)Cr<sub>2</sub>O<sub>4</sub>, (c) (Ni<sub>0.25</sub>Co<sub>0.75</sub>)Cr<sub>2</sub>O<sub>4</sub> and (d) CoCr<sub>2</sub>O<sub>4</sub>. Insets (b) and (c) show the zoomed view of the low temperature data. The  $T_C$  values were obtained using "knee-point method" similar to the results obtained for M(T) data. The solid lines in the figure are guide to eyes.

Comparison of T<sub>C</sub> values obtained using different methods.

$Ni_{1-x}Co_xCr_2O_4$ (x = 0, 0.50, 0.75, 1)	From <i>M</i> ( <i>T</i> ) data using the knee-point method Ref [15]	From $dM/dT$ versus <i>T</i> curves minimum point for 0.5 T probing field	θ <sub>f</sub> [25]	From integrated intensities using neutron diffraction data
x = 0   x = 0.50   x = 0.75   x = 1	82.4 ± 0.8 K 89.2 ± 0.7 K 90.6 ± 0.9 K 99.5 ± 0.5 K	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	76 ± 1 K 80 ± 1 K 87 ± 1 K 95 ± 1 K

particles having mostly bi-pyramidal structure with flat tops.  $M_{\rm ZFC}(T)$ and  $M_{\rm FC}(T)$  measurements at low temperature showed significant irreversibility at low temperatures with the degree of irreversibility being larger for (Ni<sub>0.5</sub>Co<sub>0.5</sub>)Cr<sub>2</sub>O<sub>4</sub> compared to (Ni<sub>0.25</sub>Co<sub>0.75</sub>)Cr<sub>2</sub>O<sub>4</sub>, indicating larger frustration. From fits of the susceptibility as a function of temperature data the ferrimagnetic Curie temperature,  $\theta_f$  or  $T_C$  of these samples were found to be 56.2  $\pm$  0.9 and 76.8  $\pm$  0.4 K, respectively. The paramagnetic Curie points  $\theta_p$  were calculated to be 73.3 and 84.9 K, respectively. The frustration index  $f = \theta_{\rm CW}/T_C$  decreased from 7.1 to 6.5 with increasing *x* from 0.5 to 0.75 that supports the claim of (Ni<sub>0.5</sub>Co<sub>0.5</sub>)Cr<sub>2</sub>O<sub>4</sub> is magnetically more frustrated. The  $T_C$  values obtained using neutron diffraction data are compared with those obtained utilizing other standard methods and found to be lower than the values obtained from the knee-point method applied to M(T) data, whilst higher than the results found from the dM/dT or  $\theta_f$ . The anomaly in temperature dependent hysteresis loops indicate that cationic substitution leads to changes in magnetic exchange interactions. Frequency dependent acsusceptibility measurements refute the possibility of spin-glass like features in these systems. These features are totally unique compared to both the NiCr<sub>2</sub>O<sub>4</sub> and CoCr<sub>2</sub>O<sub>4</sub> samples. Hence, the magnetic properties can be substantially modified by cationic substitution.

As an extension of this study, film samples of these compositions will be grown on single crystal substrates to further explore the properties dependent on composition and directional nature.



Fig. 14. ac-susceptibility as a function of temperature measured for different constant frequencies as indicated in the legend for the (a)  $(Ni_{0.5}Co_{0.5})Cr_2O_4$  and (b)  $(Ni_{0.25}Co_{0.75})Cr_2O_4$  samples.

## **Declaration of Competing Interest**

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

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# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jmmm.2019.166217.

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