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# Magnetic properties, magnetocaloric effect, and critical behaviors in $\text{Co}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$

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This research work focuses on the magnetic properties, nature of the magnetic phase transition, magnetocaloric effect, and critical scaling of magnetization of various  $\text{Co}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$  ( $x = 0, 0.125, 0.25, 0.375, \text{ and } 0.5$ ). The tunability of the magnetic moment, exchange interactions, magnetocrystalline anisotropy constant, and microwave frequency using  $\text{Cr}^{3+}$  content has been found. The nature of the magnetic phase transitions for all the  $\text{Cr}^{3+}$  concentrations exhibits as second order which has been confirmed from the analysis of critical scaling, universal curve scaling, and scaling analysis of the magnetocaloric effect. The critical exponent analysis for all samples was performed from the modified Arrott-, and Kouvel–Fisher-plots. These critical analyses suggest that  $x = 0.125, 0.250, \text{ and } 0.375$  samples show reliable results in the magnetocaloric effect with relative cooling power (RCP) values in the range of  $128\text{--}145 \text{ J kg}^{-1}$ . On the other hand,  $x = 0.00, \text{ and } 0.500$  samples exhibit inconsistent RCP values. The universal curve scaling also confirms the reliability of the magnetocaloric effect of the investigated samples.

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## 1 Introduction

Over the past few decades, research on iron oxide compounds like spinel ferrite, hexaferrite, and garnet has become a topic of discussion among scientists, due to their attractive practical applications in magneto-sensing devices, and biotechnology.<sup>1–7</sup> These key topics attracted scientists because these types of compounds exhibit unique magnetic and magnetocaloric effects (MCE).<sup>1–3,8–10</sup> Among all the ferrites,  $\text{CoFe}_2\text{O}_4$  (COF) has been focused on in recent years by academia, the medical sector, and industry due to its remarkable magnetic and MCE properties.<sup>11–19</sup> The structural, magnetic, and MCE properties of COF can be tuned by doping/substituting divalent or trivalent cations.<sup>11,18–24</sup> The tunability of structural parameters due to  $\text{Cr}^{3+}$  substitution in stoichiometric and non-stoichiometric COF is reported in our earlier literature.<sup>25</sup> It was observed that there are structural defects due to  $\text{Cr}^{3+}$  substitution. In recent years, a large number of articles have been found on the study of magnetic field ( $H$ ) and temperature ( $T$ ) dependent magnetization ( $M$ ) of various ferrites.<sup>1,4,26,27</sup> Massoudi *et al.* have observed the non-collinear model on Ni–Zn–Al ferrite by comparing the theoretical and experimental magnetic moment calculated from the cation distribution and M–H hysteresis curve, respectively.<sup>1</sup> The paramagnetic moment followed by the Curie–Weiss law and magnetic phase transition temperature has been studied from the field cooled (FC) and zero fields cooled (ZFC) magnetization.<sup>23,28</sup> Spinel ferrites also attracted scientists across

the world due to their interesting MCE properties.<sup>4,29–32</sup> The MCE is an intrinsic thermodynamic property of magnetic materials that causes a change in the temperature of the substance under the action of a magnetic field.<sup>33</sup> In various literature, the MCE of such materials has been studied from the isothermal M–H over a wide temperature range near the magnetic phase transition.<sup>4,34</sup> The MCE values have been calculated from the change of magnetic entropy from the isothermal M–H curve based on Maxwell's thermodynamic relation.<sup>34,35</sup> The nature of magnetic phase transition has also been reported in various literature extracted from the isothermal M–H curves using the Arrott plot,<sup>36</sup> and the Arrott–Noakes model.<sup>37</sup> Law *et al.* have studied the nature of magnetic phase transition by calculating a critical exponent  $n$  from the change of entropy as a function of temperature.<sup>38</sup> Various reports have been conducted on the analysis of critical exponents to confirm the universal class of materials.<sup>32,34</sup> Franco *et al.* have first reported the phenomenological universal scaling curve taking the normalized entropy change as a function of rescaled temperature.<sup>39</sup>

In this research, the effect of  $\text{Cr}^{3+}$  substitution on magnetic and MCE properties of various  $\text{Co}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$  ( $x = 0, 0.125, 0.25, 0.375, \text{ and } 0.5$ ) have been studied. A detailed investigation of magnetic properties has been carried out by analyzing the M–H hysteresis and FC-ZFC magnetization behaviors. The MCE properties of  $\text{Cr}^{3+}$  substituted cobalt ferrite have been investigated by analyzing the M–H isotherms. The nature of magnetic phase transition has also been examined by analyzing the Arrott plot. The nature of the universal class of these materials has been analyzed by calculating the critical exponent followed by

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the modified Arrott plot (MAP), the Kouvel–Fisher method, and critical isotherm analysis. Finally, the reliability of the MCE properties and universal class have been studied in detail using as usual methods.

## 2 Experimental

The nominal chemical compositions  $\text{Co}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$  ( $x = 0, 0.125, 0.25, 0.375, \text{ and } 0.5$ ) have been synthesized by the standard solid-state reaction technique. The stoichiometric amount of  $\text{Co}_2\text{O}_3$  (98.0%),  $\text{Cr}_2\text{O}_3$  (99.9%), and  $\text{Fe}_2\text{O}_3$  (96.0%) have been mixed in a mortar with a pestle. After completing the mixing process for 2 hours for each composition, the mixtures were crushed using a planetary ball mill (MSK-SFM-1) for 12 h. To complete the solid-state reaction the milled powder has been calcined at  $800^\circ\text{C}$  for 6 h. Then the calcined powder of each composition has been pressed in the form of a pellet using

a uniaxial pressure of 16 000 psi and then sintered at  $1200^\circ\text{C}$  for 6 h. Then a part of sintered pellets was re-crushed into fine powder for performing X-ray diffraction (XRD) to confirm the formation of spinel-type ferrite. The results of phase formation have been reported elsewhere.<sup>25</sup> After confirming the formation of spinel-type ferrites, these compositions are subjected to further investigation of their magnetic properties. The FC and ZFC magnetization were performed for the measurement of the phase transition temperature. The M–H hysteresis loop measurements were performed at room temperature for saturation magnetization and other relevant parameters, The M–H isotherms at a various temperatures above and below the magnetic phase transition for each composition have been conducted by using Quantum Design MPMS3 SQUID magnetometer. Then the MCE properties and critical scaling have been analyzed for each composition using standard method described in Section 3.4.

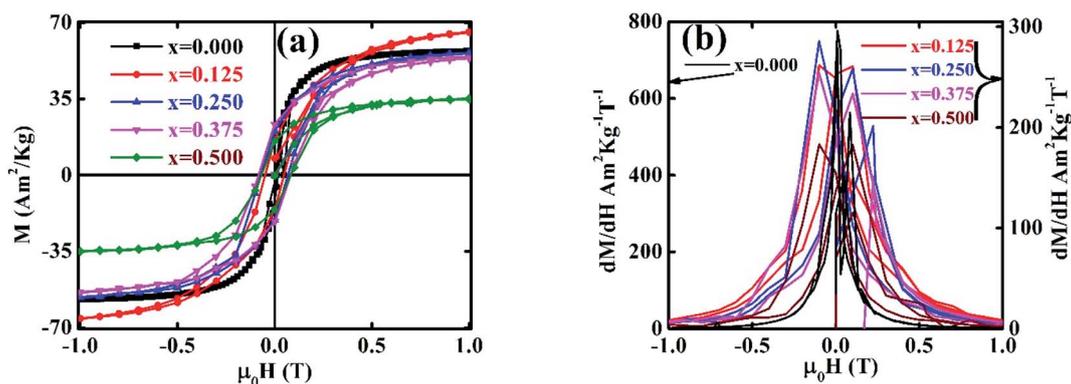


Fig. 1 (a) The room temperature M–H hysteresis loops for various  $\text{Co}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ . (b) The  $dM/dH$  versus  $H$  plots for various  $\text{Co}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ .

Table 1 Magnetic parameters obtained from M–H hysteresis loops, and M–T curve for various  $\text{Co}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$

Various parameters	$x$				
	0.000	0.125	0.250	0.375	0.500
$\theta_{\text{cw}}$ (K)	636	720	710	707	810
$C$	2.46	1.15	0.89	0.84	0.35
$T_{\text{C}}$ (K)	675	740	735	731	687
$T_{\text{B}}$ (K)	631	685	680	677	671
$M_{\text{s}}$ ( $\text{A m}^2 \text{ kg}^{-1}$ )	58	70	59	57	37
$M_{\text{r}}$ ( $\text{A m}^2 \text{ kg}^{-1}$ )	01	19	20	23	15
$H_{\text{c}}$ (T)	0.02	0.05	0.07	0.08	0.07
$K$ ( $\text{J m}^{-3}$ )	1.44	3.6	4.2	4.6	2.2
$\sigma_{\text{w}}$ (J)	$6 \times 10^{-6}$	$9 \times 10^{-6}$	$10 \times 10^{-6}$	$11 \times 10^{-6}$	$8 \times 10^{-6}$
$D_{\text{m}}$ (nm)	78	33	32	31	26
$R$	0.02	0.268	0.273	0.277	0.306
$M_{\text{A}}$ ( $\mu_{\text{B}}$ )	5.8	5.7	5.6	5.5	5.4
$M_{\text{B}}$ ( $\mu_{\text{B}}$ )	10.01	10.07	10.17	10.25	10.34
$n_{\text{B}}$ ( $\mu_{\text{B}}$ )	2.45	2.94	2.45	2.37	1.51
$n_{\text{th}}$ ( $\mu_{\text{B}}$ )	4.23	4.37	4.56	4.74	4.95
$\mu_{\text{eff}}^{\text{exp}}$ ( $\mu_{\text{B}}$ )	4.43	3.03	2.66	2.59	1.71
$\alpha_{\text{YK}}$ (deg.)	35	31	38	40	48
$J$ ( $\text{J k}^{-1}$ )	$1.55 \times 10^{-21}$	$1.7 \times 10^{-21}$	$1.69 \times 10^{-21}$	$1.68 \times 10^{-21}$	$1.58 \times 10^{-21}$
$\omega_{\text{m}}$ (GHz)	12.9	15.6	13.0	12.6	8.1



### 3 Results and discussion

#### 3.1 Structural analysis

The all samples of  $\text{Co}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$  exhibit single-phase cubic spinel structure with a space group of  $Fd\bar{3}m$ . The details of crystal structure, with cation distribution, have been explored, and results are already published in ref. 25.

#### 3.2 Magnetic properties

The saturation magnetization ( $M_s$ ), remanent magnetization ( $M_r$ ), and coercivity ( $H_c$ ) are the most important parameters for a material to know its magnetic behavior. In general magnetization *vs.* applied magnetic field ( $M$ -) hysteresis loop provide

a reliable information about  $M_s$ ,  $M_r$ , and  $H_c$ . The  $M$ - $H$  hysteresis loops for all samples have been illustrated in Fig. 1(a). From  $M$ - $H$  hysteresis loops the values of  $M_s$ ,  $M_r$ , and  $H_c$  are extracted and listed in Table 1. From the Table 1, it evident that there is a decreasing trend of  $M_s$  with increasing  $\text{Cr}^{3+}$  content. However,  $H_c$  and  $M_r$  show the increasing trend up to  $x = 0.375$  then it decreases for further increase of  $x$ . The decreasing trend of  $M_s$  may be due to the abnormal grain growth and pore blockage. The increasing trend of  $H_c$  is perhaps due to the decrease in crystallite size ( $D$ ) as calculated from the XRD data.<sup>25</sup> For  $x = 0.500$ , the  $H_c$  value does not shows the corresponding behavior as crystallite size which may be due to the excess ion as explained in the literature. To know the inter-grain exchange mechanism, the

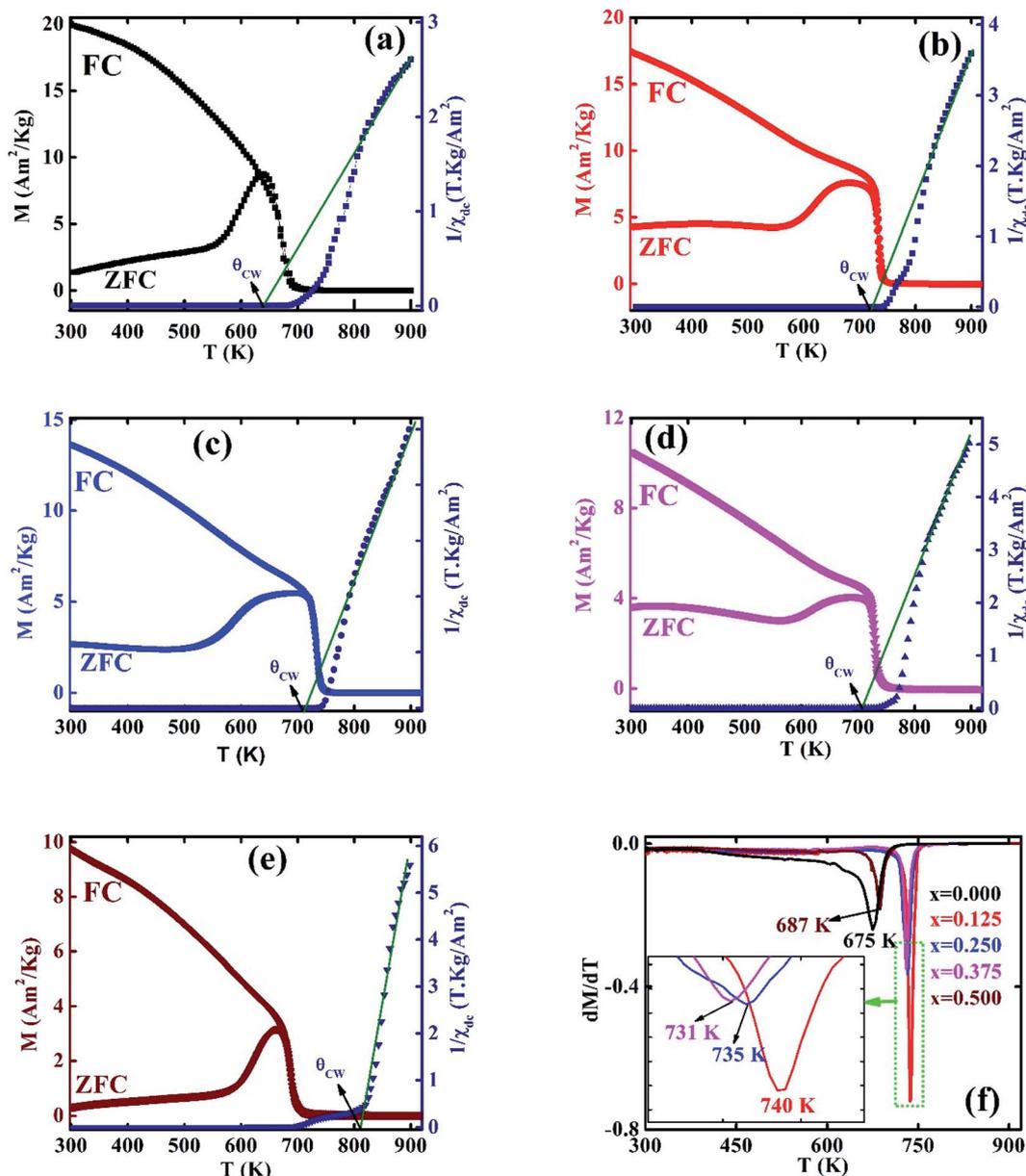


Fig. 2 The temperature dependence of FC and ZFC magnetization (left axis) and the inverse susceptibility (right axis) for various  $\text{Co}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$  (a)  $x = 0.0$ , (b)  $x = 0.125$ , (c)  $0.25$ , (d)  $0.375$ , and (e)  $x = 0.500$ . (f) The  $dM/dT$  vs.  $T$  plots for various  $\text{Co}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ .



calculation of remanence ratio  $R (= M_r/M_s)$  is most important. The calculated  $R$  values (Table 1) show less than 0.5 which indicates the existence of magnetic dipole interaction with random orientation.<sup>40</sup> According to Stoner–Wohlfarth theory, the anisotropy constant ( $K$ ) value is related to the coercivity has been calculated using the following expression:<sup>41</sup>

$$K = \frac{M_s H_c}{0.98} \quad (1)$$

The calculated  $K$  values for all the Cr concentrations are tabulated in Table 1. It is observed from the Table 1 that  $K$  values increase with increasing Cr content up to  $x = 0.375$ , indicating the increase of domain wall energy. Then it shows

the decreasing value which may be due to the excess ions showing negative values of the vacancy parameter as explained in the literature.<sup>25</sup> The domain wall energy ( $\sigma_w$ ) can be calculated using the following expression:<sup>42</sup>

$$\sigma_w = \left( \frac{2k_B T_C K}{a} \right)^{\frac{1}{2}} \quad (2)$$

where  $k_B$  is Boltzmann constant,  $T_C$  is Curie temperature and  $a$  is the lattice constant. The calculated domain wall energy for all samples has been tabulated in Table 1. From Table 1 the values for  $\sigma_w$  are found to be increasing with the increase of Cr content up to  $x = 0.375$  then it shows a decreasing trend.

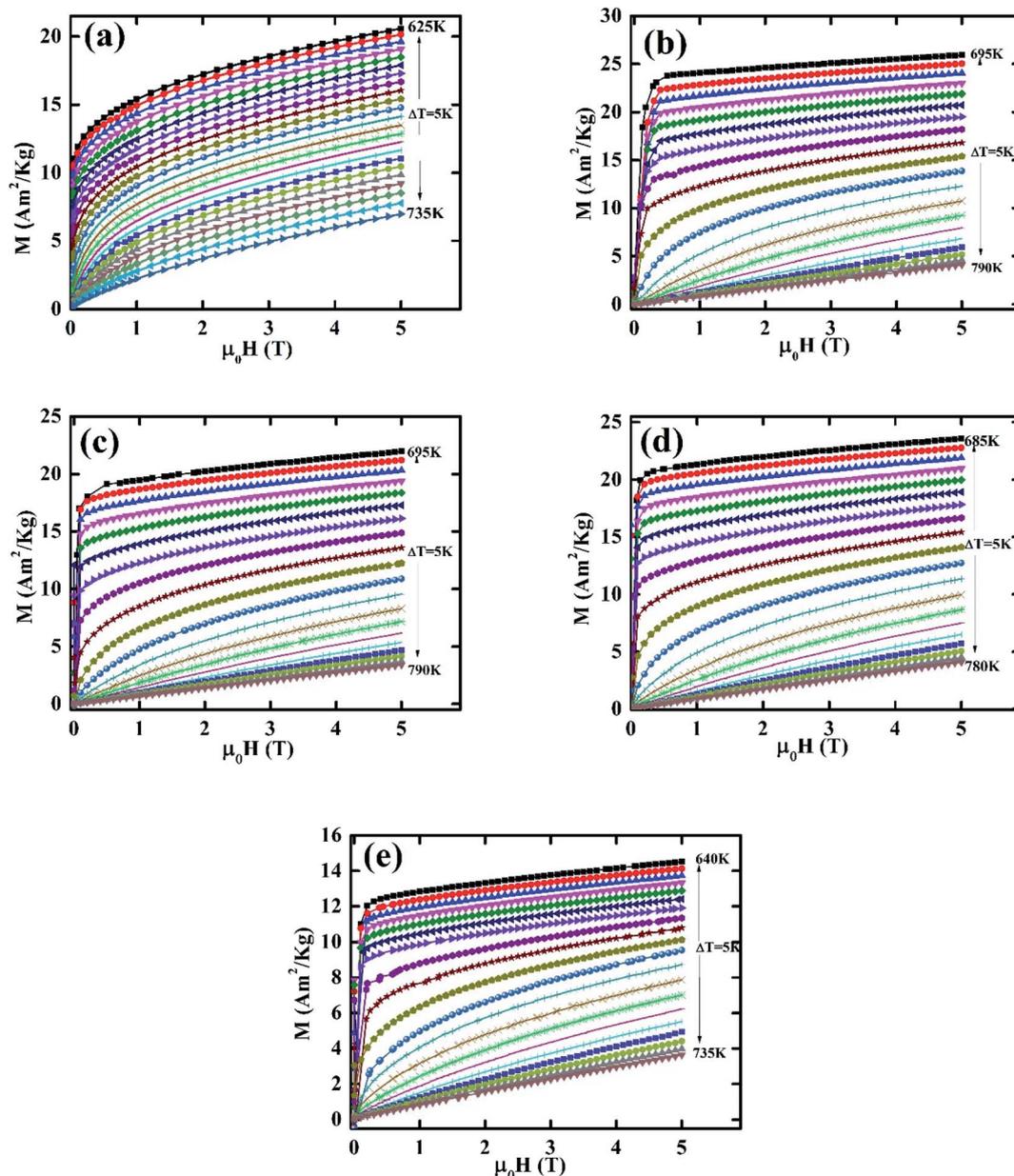


Fig. 3 M–H isotherm for various  $\text{Co}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ . (a)  $x = 0.0$ , (b)  $x = 0.125$ , (c)  $0.25$ , (d)  $0.375$ , and (e)  $x = 0.500$ .



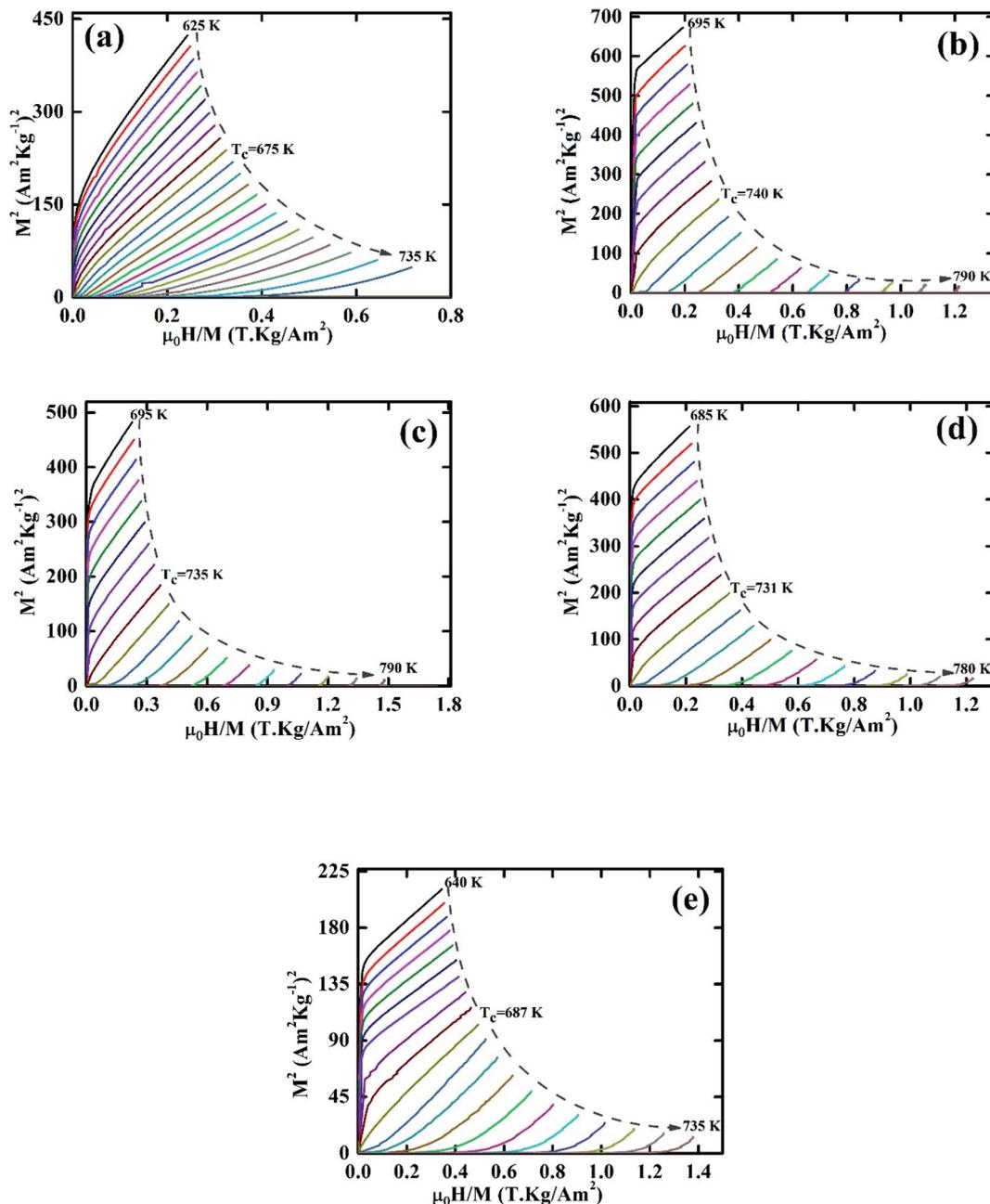


Fig. 4 Arrott plots for various  $\text{Co}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ . (a)  $x = 0.0$ , (b)  $x = 0.125$ , (c)  $0.25$ , (d)  $0.375$ , and (e)  $x = 0.500$ .

To know the domain type of materials, the illustration of the  $dM/dH$  versus  $H$  plot is most important.<sup>40</sup> The  $dM/dH$  versus  $H$  for all samples have been depicted in Fig. 1(b). Multiple broad peaks near the zero magnetic field observed for all samples indicate multi magnetic domain. To know the agreeable domain nature, determination of critical size by using the following expression is most important:<sup>43</sup>

$$D_m = \frac{9\sigma_w}{2\pi M_{SP}^2} \quad (3)$$

where,  $M_{SP}$  is spontaneous magnetization. For all samples  $D_m$  (Table 1) shows a lower value than the calculated  $D$  values from

XRD,<sup>25</sup> which follows the particle spherical model. The  $D_m < D$  for all samples reveals that the nanocrystallites have an incipient structure of magnetic domains.<sup>43</sup>

The cation distribution results as presented in our previous article<sup>25</sup> clearly indicate that both  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  occupy the tetrahedral (A) and octahedral (B) sites, respectively whereas  $\text{Fe}^{3+}$  occupied both the A- and B-sites for  $x = 0$ . However, for  $x = 0.125$  to  $0.500$ , the  $\text{Cr}^{3+}$  is found in both the A- and B-sites in place of  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$ , respectively. The calculated magnetic moment  $M_A$  and  $M_B$  for A- and B-sites are tabulated in Table 1. From Table 1 the values of  $M_A$  are found to be decreasing with an increase of  $\text{Cr}^{3+}$  which is due to the less magnetic moment of



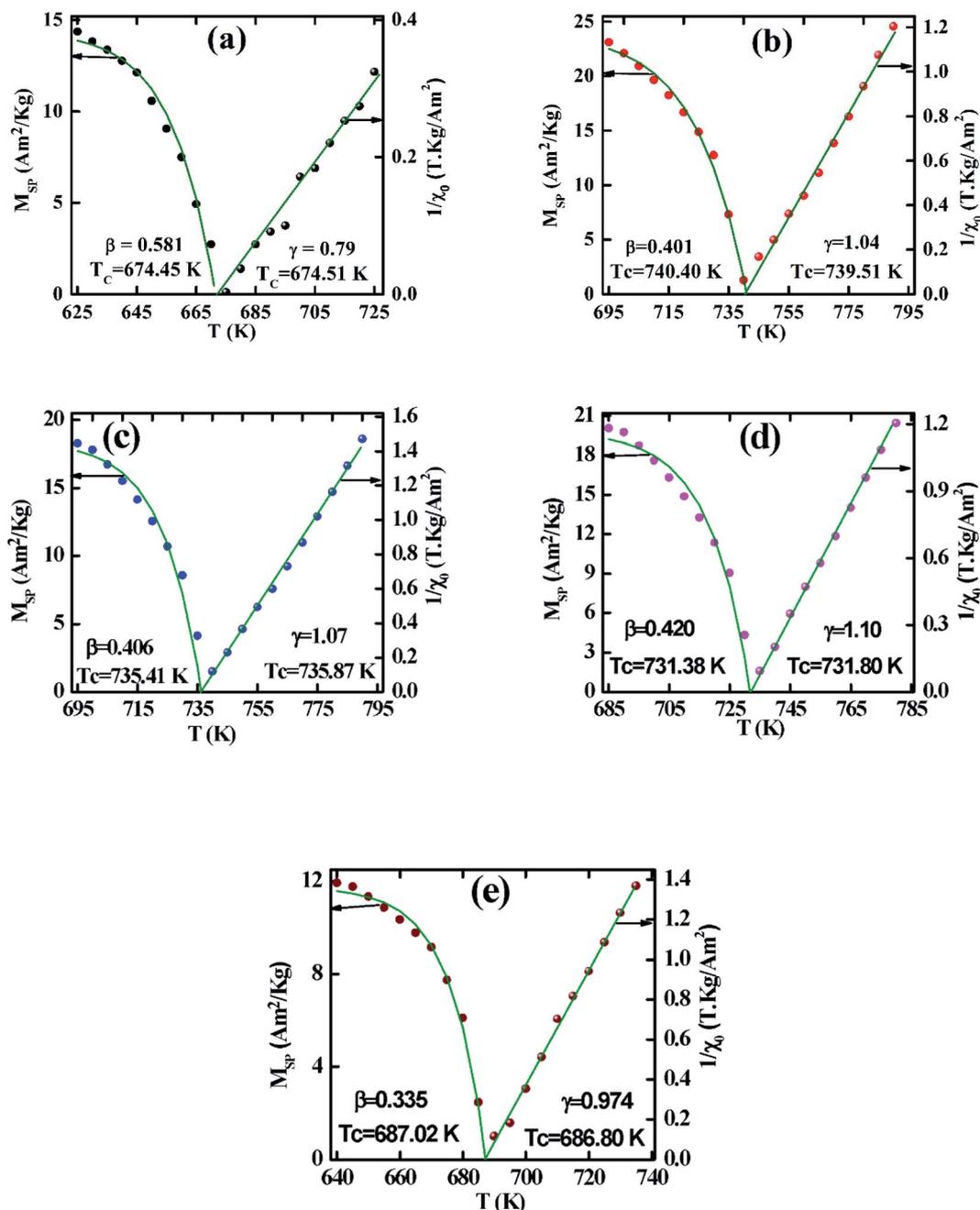


Fig. 5 Spontaneous magnetization  $M_{SP}$  and zero field inverse susceptibility  $\chi_0^{-1}$  as a function of temperature for various  $\text{Co}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ . (a)  $x = 0.0$ , (b)  $x = 0.125$ , (c) 0.25, (d) 0.375, and (e)  $x = 0.500$ .

$\text{Cr}^{3+}$  ( $3.87 \mu_B$ ) than  $\text{Co}^{2+}$  ( $4.87 \mu_B$ ). But the values of  $M_B$  are found to be increasing due to an increase of  $\text{Fe}^{3+}$  with a magnetic moment of  $5.92 \mu_B$ . The net theoretical magnetic moment calculated by using  $n_{th} = M_B - M_A$  relation accordingly to Néel's co-linear model is tabulated in Table 1. From Table 1, it is observed that the net magnetic moment show an increasing trend which shows inconsistency with the experimental  $M_s$ . To know the reason behind the inconsistency the experimental number of Bohr magneton ( $n_B$ ) is calculated from the value of  $M_s$  using the following expression:<sup>1</sup>

$$n_B = \frac{MM_s}{5585\mu_B} \quad (4)$$

where,  $M$  is the molecular weight. The calculated values of  $n_B$  are also tabulated in Table 1, where lower values of  $n_B$  compared to that of  $n_{th}$  are evident which suggests that Néel's collinear model is not agreeable for the synthesized samples. For this reason, Yafet-Kittel (YK) non-collinear model is considered to explain the deviation between  $n_{th}$  and  $n_B$ . According to the YK non-collinear model, the Yafet-Kittel angle ( $\alpha_{YK}$ ) can be calculated using the following equation:<sup>1</sup>



**Table 2** The obtained values of critical exponents ( $\beta$ ,  $\gamma$ , and  $\delta$ ) and  $T_C$ s from the modified Arrott plot (MAP), Kouvel–Fisher (KF) plot, critical isotherm, Widom scaling, magnetocaloric effect, and relative cooling power (RCP) analysis across the PM–FM transition region for various  $\text{Co}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$

$x$	$\beta$	$\gamma$	$\delta$	$n$	$T_C$ (K)	Methods	
0.000	0.581	0.79	—	—	674.45	MAP	
					674.51		
	0.325	1.17	—	0.231	673.37	KF	
					673.42		
	—	—	3.23	—	—	Critical isotherm	
0.125	—	—	2.34	—	—	MCE/RCP	
	—	—	—	0.910	675	$ \Delta S_m^{\max} $	
	—	—	2.36	—	—	Widom scaling	
	0.401	1.04	—	—	740.4	MAP	
					739.5		
	0.461	0.998	—	0.676	740.12	KF	
					740.09		
	—	—	3.61	—	—	Critical isotherm	
	—	—	3.64	—	—	MCE/RCP	
	—	—	—	0.677	740	$ \Delta S_m^{\max} $	
0.250	—	—	3.59	—	—	Widom scaling	
	0.406	1.07	—	—	735.41	MAP	
					735.87		
	0.464	1.03	—	0.685	734.92	KF	
					735.09		
	—	—	3.62	—	—	Critical isotherm	
	—	—	3.65	—	—	MCE/RCP	
	—	—	—	0.690	735	$ \Delta S_m^{\max} $	
	—	—	3.63	—	—	Widom scaling	
	0.375	0.42	1.1	—	—	731.38	MAP
					731.80		
0.466		1.01	—	0.682	731.32	KF	
					730.89		
—		—	3.60	—	—	Critical isotherm	
—		—	3.61	—	—	MCE/RCP	
—		—	—	0.679	731	$ \Delta S_m^{\max} $	
—		—	3.62	—	—	Widom scaling	
0.500		0.335	0.974	—	—	687.02	MAP
						686.80	
	0.331	1.08	—	0.422	686.85	KF	
					686.89		
	—	—	3.50	—	—	Critical isotherm	
	—	—	4.43	—	—	MCE/RCP	
	—	—	—	0.501	687	$ \Delta S_m^{\max} $	
	—	—	3.91	—	—	Widom scaling	

$$\cos \alpha_{\text{YK}} = \frac{n_{\text{B}} + M_{\text{A}}}{M_{\text{B}}} \quad (5)$$

The  $\alpha_{\text{YK}}$  values for all the samples are found to be in the range of 30 to 50° (Table 1) which confirms the non-collinear spin structure that indicates triangular spin arrangement in the B-sites. The lower values of  $\text{Cr}^{3+}$  substitution indicate the decreasing trend of  $\alpha_{\text{YK}}$  but at higher values of  $\text{Cr}^{3+}$  enhance the  $\alpha_{\text{YK}}$ . Although decreasing and increasing trends are evident but they do not show zero  $\alpha_{\text{YK}}$ . Therefore, the nonzero YK angle suggest that synthesized samples show YK magnetic ordering. The variation of  $\alpha_{\text{YK}}$  with Cr concentration also support the change in Curie temperature ( $T_C$ ) as evident from Fig. 2.

The FC and ZFC magnetization plots for all samples were recorded in the presence of 10 mT field in the temperature range of 300–900 K as shown in Fig. 2 (a–e left Y axis). It is evident that the magnetization ( $M$ ) value in case of ZFC increases up to maximum at a certain temperature for all samples called blocking temperature ( $T_B$ ) then it shows a decreasing trend with an increase of temperature while the FC magnetization decreases very slowly up to  $T_C$ , then a sharp fall is observed for both cases. The values of  $T_B$  of all samples are tabulated in Table 1 where maximum  $T_B$  value is observed for  $x = 0.125$ . To know the exact  $T_C$  values  $dM/dT$  vs.  $T$  graphs are illustrated in Fig. 2(f), where a single peak for all samples confirms the single transition at  $T_C$  without showing any spin frustration. The  $T_C$  values are presented in Table 1. It is observed that  $T_C$  show a maximum for  $x = 0.125$ . With an increase in Cr content, there is a decrease in  $T_C$  values. The variation of  $T_C$  values and  $\alpha_{\text{YK}}$  angles of these compositions may be explained by the increasing and decreasing trend of calculated exchange interaction ( $J$ ) using the following equation:

$$J = \frac{3k_{\text{B}}T_{\text{C}}}{2z \times s(s+1)} \quad (6)$$

where  $z$  is the coordination number ( $= 12$ ) and  $s = \frac{1}{2}$ . The values of  $J$  are presented in Table 1.

The inverse magnetic susceptibility ( $\chi^{-1}$ ) as a function of temperature ( $T$ ) is depicted in Fig. 2 (a–e right Y axis) for all samples. From Fig. 2(a–e) it is found that the  $\chi^{-1}$  rises sharply when the magnetic state changes from the ferromagnetic to paramagnetic. In the paramagnetic region, susceptibility data follow the Curie–Weiss (CW) expression<sup>34</sup>

$$\chi(T) = \frac{C}{T - \Theta_{\text{CW}}} \quad (7)$$

where  $C$  is the Curie constant which can be obtained from the slope of the linear fit of  $\chi^{-1}$  vs.  $T$  graph (Fig. 2) and  $\Theta_{\text{CW}}$  is the CW temperature that also can be obtained from Fig. 2. The calculated values of  $C$ , and the estimated values of  $\Theta_{\text{CW}}$  from the graphs are listed in Table 1. The estimated values  $\Theta_{\text{CW}}$  are found to be lower than that of  $T_C$  for the compositions up to  $x = 0.375$  which corresponds to the presence of long-range order. However, for  $x = 0.500$  the value of  $\Theta_{\text{CW}}$  is found to be a larger than that of  $T_C$  which corresponds to the short-range order which may originate from the excess ion. The experimental effective magnetic moment has been calculated by using  $C$  values according to the following expression:<sup>1</sup>

$$\mu_{\text{eff}}^{\text{exp}} = \sqrt{8C} \mu_{\text{B}} \quad (8)$$

The calculated values of  $\mu_{\text{eff}}^{\text{exp}}$  are tabulated in Table 1 where the decreasing trend of  $\mu_{\text{eff}}^{\text{exp}}$  with an increase of Cr content has been observed. The decrease in  $\mu_{\text{eff}}^{\text{exp}}$  with the increase of  $\text{Cr}^{3+}$  content may refer to the decrease in ferromagnetic clusters present in the paramagnetic phase.<sup>2</sup>

The microwave frequency ( $\omega_{\text{m}}$ ) is an important parameter for any materials for high-frequency microwave applications. The  $\omega_{\text{m}}$  can be evaluated by using the following expression:<sup>1,2</sup>



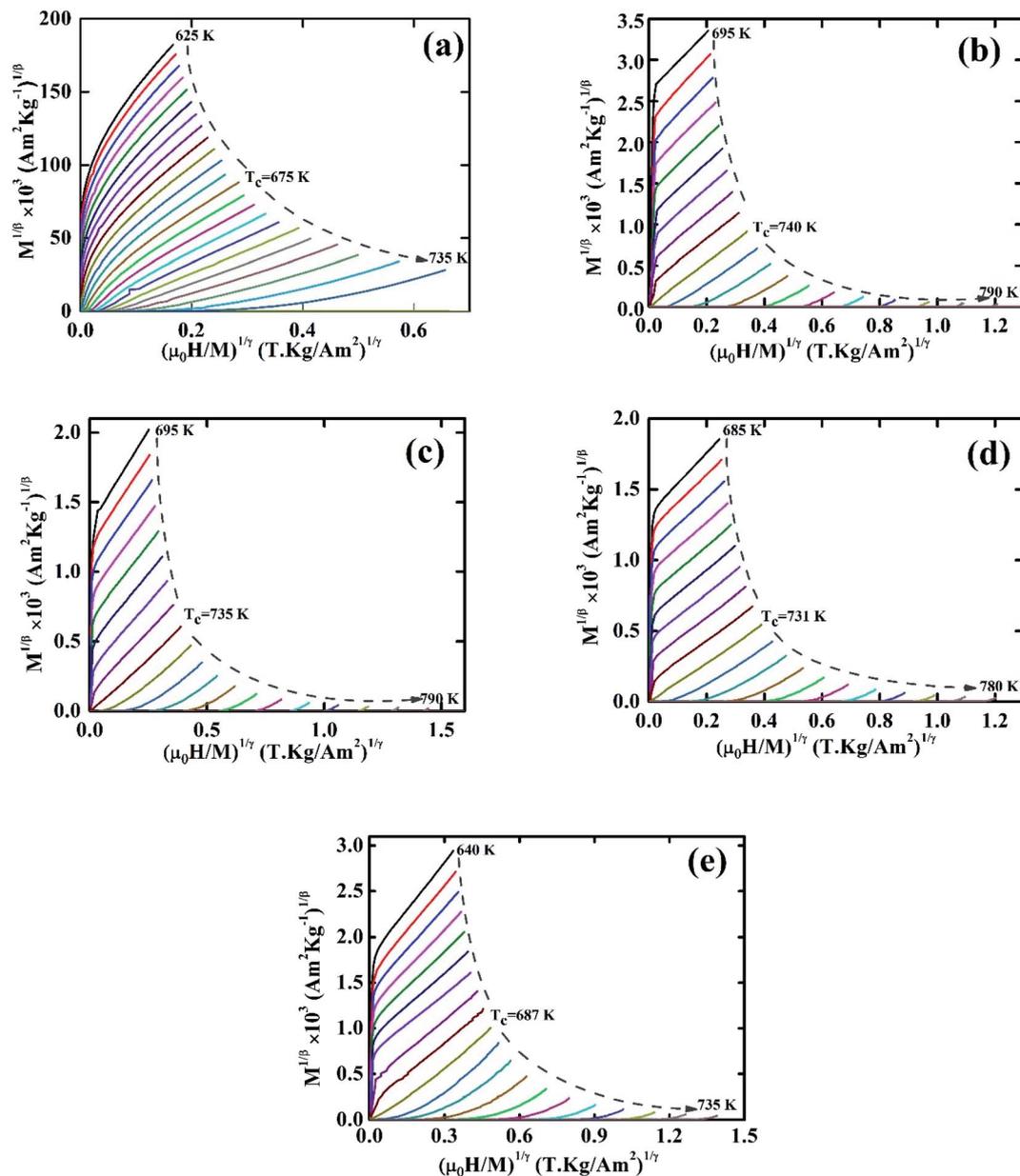


Fig. 6 Modified Arrott plot for various  $\text{Co}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ . (a)  $x = 0.0$ , (b)  $x = 0.125$ , (c)  $0.25$ , (d)  $0.375$ , and (e)  $x = 0.500$ .

$$\omega_m = \gamma_1 8\pi^2 M_s \quad (9)$$

where  $\gamma_1$  is the gyromagnetic ratio ( $\gamma_1 = 2.8 \text{ MHz Oe}^{-1}$ ). The calculated  $\omega_m$  values are tabulated in Table 1, where maximum value is observed for  $x = 0.125$ . The calculated  $\omega_m$  values are in the range of 8.1–15.6 GHz which is higher than that of previously reported values.<sup>1,2</sup> Thus, it is affirmed that synthesized compositions may be a good candidate for high-frequency microwave applications such as satellite communications and biomedical applications.<sup>44</sup>

### 3.3 Critical scaling

**3.3.1 Modified Arrott plot.** The critical analysis is most important for any inorganic material close to the phase

transition. The critical behavior has been conducted by measuring the magnetization isotherms ( $M$ - $H$ ) close to the respective  $T_c$  following the procedure described in ref. 4 and 34. The  $M$ - $H$  isotherms for all samples are illustrated in Fig. 3. The non-linear  $M$ - $H$  behavior below  $T_c$  confirms the compositions are ferromagnetic (FM), and the linear  $M$ - $H$  behavior above  $T_c$  confirms paramagnetic (PM) nature. Based on the Landau theory, the Gibbs free energy can be written as.<sup>45</sup>

$$G(M, T) = G_0 + \frac{1}{2}A_1M^2 + \frac{1}{4}A_2M^4 + \frac{1}{6}A_3M^6 + \dots - \mu_0H \quad (10)$$

where,  $A_1$ ,  $A_2$ , and  $A_3$  are Landau co-efficient. Neglecting the higher-order terms the above equation can be written as



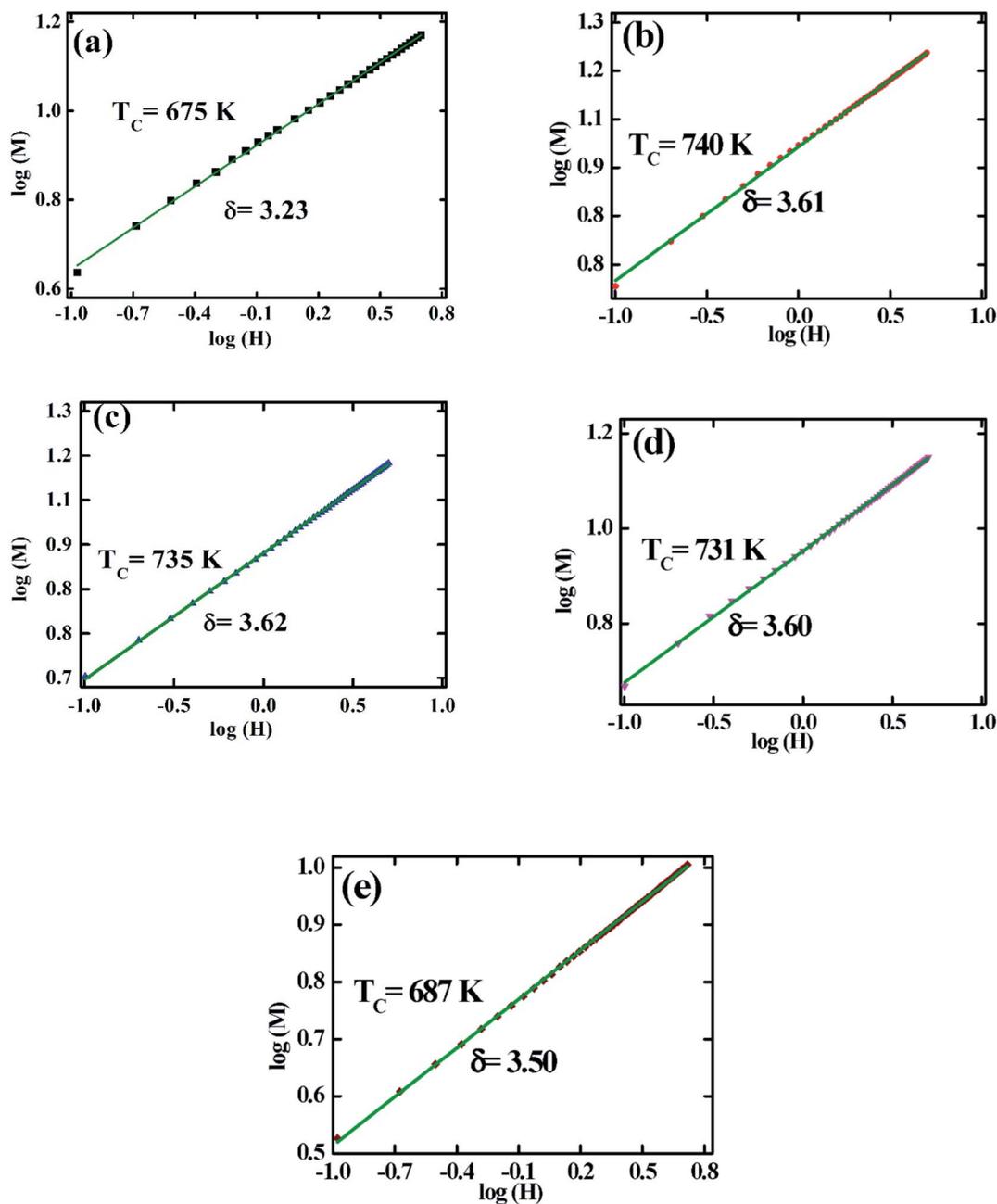


Fig. 7 The log–log plot of isothermal magnetization ( $M$ ) vs. applied field ( $H$ ) for various  $\text{Co}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ . (a)  $x = 0.0$ , (b)  $x = 0.125$ , (c)  $0.25$ , (d)  $0.375$ , and (e)  $x = 0.500$ .

$$G(M, T) = G_0 + \frac{1}{2}A_1M^2 + \frac{1}{4}A_2M^4 - \mu_0H \quad (11)$$

At the equilibrium condition,  $\frac{\partial G}{\partial M} = 0$ ; then the magnetic equation of state can be written as

$$\frac{\mu_0H}{M} = A_1 + A_2M^2 \quad (12)$$

The nature of FM-PM phase transition may be determined from the  $M^2$  vs.  $\mu_0H/M$ , known as Arrott plot.<sup>36</sup> The Arrott plots

for all samples are depicted in Fig. 4. No negative slope has been found in Fig. 4, which confirms the second-order phase transition. It is worth noting that  $M^2$  versus  $\mu_0H/M$  plot should follow the equation of straight line passes through the origin. However, the above-mentioned behavior is not observed for all samples. Therefore, further analysis is performed for assumed second-order FM-PM phase transition using modified Arrott plots (MAP) according to Arrott–Noakes<sup>37</sup> as mentioned by the following expression:

$$\left(\frac{\mu_0H}{M}\right)^{\frac{1}{\gamma}} = A_1 \frac{T - T_c}{T_c} + A_2M^{\frac{1}{\beta}} \quad (13)$$



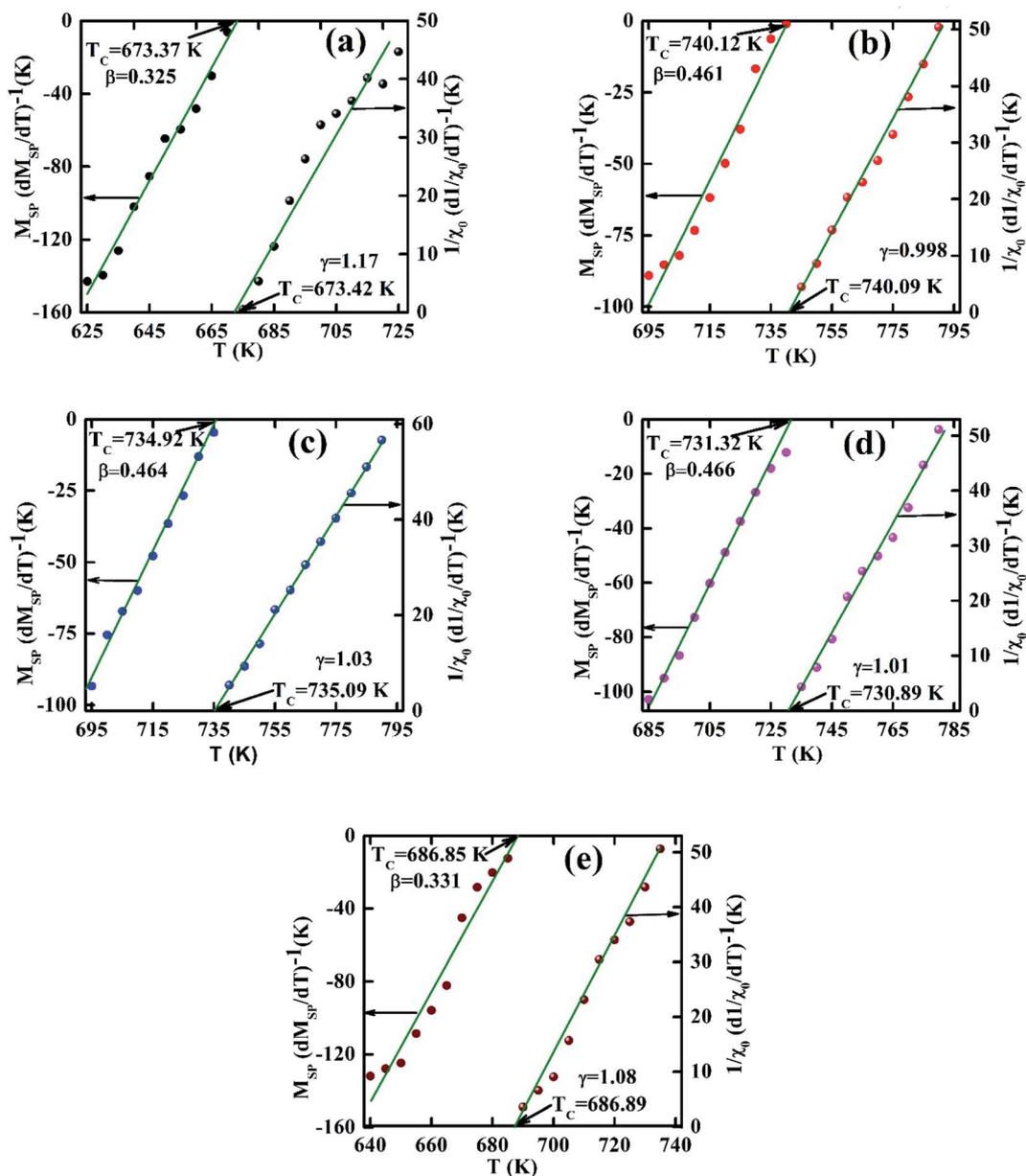


Fig. 8 Kouvel–Fisher plots  $M_{SP}$  and  $\chi_0^{-1}$  as a function of temperature for various  $\text{Co}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ . (a)  $x = 0.0$ , (b)  $x = 0.125$ , (c)  $0.25$ , (d)  $0.375$ , and (e)  $x = 0.500$ .

where  $\beta$ , and  $\gamma$  are the critical exponents.

The set of critical exponents ( $\beta$ ,  $\gamma$ , and  $\delta$ ) are calculated by analyzing spontaneous magnetization ( $M_{SP}$ ), zero-field susceptibility ( $\chi_0$ ), and magnetization isotherm at the  $T_C$  using the following power-laws:<sup>4,34</sup>

$$M_{SP}(T) = M_0(-\varepsilon)^\beta, \text{ for } \varepsilon < 0, T < T_C, \quad (14)$$

$$\chi_0(T) = I(\varepsilon)^\gamma, \text{ for } \varepsilon > 0, T > T_C \quad (15)$$

$$M = D_1(\mu_0 H)^{1/\delta}, \text{ for } \varepsilon = 0, T = T_C \quad (16)$$

$$M(\mu_0 H, \varepsilon)|\varepsilon|^{-\beta} = f_{\pm}\mu_0 H|\varepsilon|^{-(\beta+\gamma)} \quad (17)$$

where,  $\varepsilon = \frac{T - T_C}{T_C}$  is the reduced temperature,  $M_0$ ,  $I$ , and  $D_1$  are the critical coefficients, and  $f_+$  and  $f_-$  are the scaling functions above and below  $T_C$ , respectively.

To calculate the values of  $\beta$  and  $\gamma$  (using eqn (14) and (15)) the  $M_{SP}$  vs.  $T$ , and  $1/\chi_0$  vs.  $T$  are presented in Fig. 5. From Fig. 5 the  $\beta$  and  $\gamma$  values are estimated from the fitting curve for all the samples that have been tabulated in Table 2. From Table 2 it is found that the values of  $\beta$  and  $\gamma$  are close to the values of the mean-field model for the samples  $x = 0.125$ ,  $0.250$ ,  $0.375$ , however, for  $x = 0$  and  $x = 0.5$ , there is a large difference that affects the MCE values as explained in the Section 3.4. The  $T_C$  values are also calculated from the fitting curve of Fig. 5 which



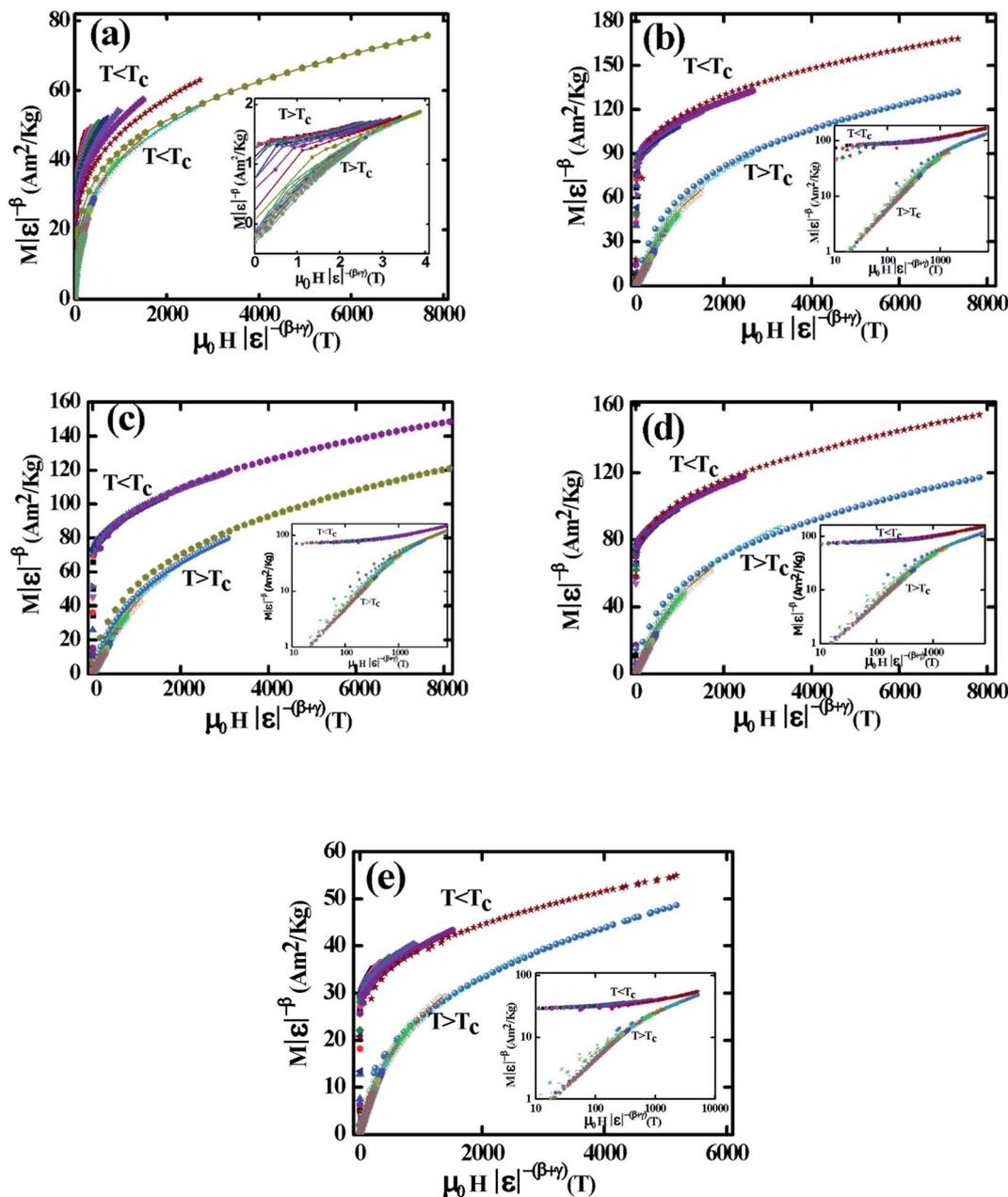


Fig. 9 Scaling plots below and above  $T_c$  values using  $\beta$  and  $\gamma$  estimated using the Kouvel–Fisher method. Insets show plots in the log–log scale for various  $\text{Co}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ . (a)  $x = 0.0$ , (b)  $x = 0.125$ , (c)  $0.25$ , (d)  $0.375$ , and (e)  $x = 0.500$ .

also has been tabulated in Table 2 and the values are close to that obtained from M–T measurements described in Section 3.2. The  $M^{\frac{1}{\beta}}$  vs.  $\left(\frac{\mu_0 H}{M}\right)^{\frac{1}{\gamma}}$  graphs (MAP) for all samples are presented in Fig. 6 using the  $\beta$ , and  $\gamma$  values extracted from Fig. 5. These MAP plots show the straight line that passes through the origin at  $T_c$  for  $x = 0.125, 0.25, 0.375$ , and  $0.500$  which satisfy the required condition discussed earlier, however,  $x = 0$  shows dissimilar behavior.

The variation in the critical isotherm  $M(T_c, H)$  can be described by a power-law (eqn (16)) characterized by the critical exponent  $\delta$ . The critical exponent  $\delta$  has been obtained from the

inverse of slopes of  $M(T_c)$  vs.  $H$  curve in the log–log scale as shown in Fig. 7. The  $\delta$  values are also determined from the previously calculated  $\beta$ , and  $\gamma$  values according to statistical theory using Widom relation:<sup>46</sup>

$$\delta = 1 + \frac{\gamma}{\beta} \quad (18)$$

The estimated  $\delta$  values according to the above two cases for all samples are tabulated in Table 2. The  $\delta$  values for both cases are close to each other for the sample for  $x = 0.125, 0.25$ , and  $0.375$  universal class. But for  $x = 0.00$ , and  $0.500$  the  $\delta$  values do not match each other.



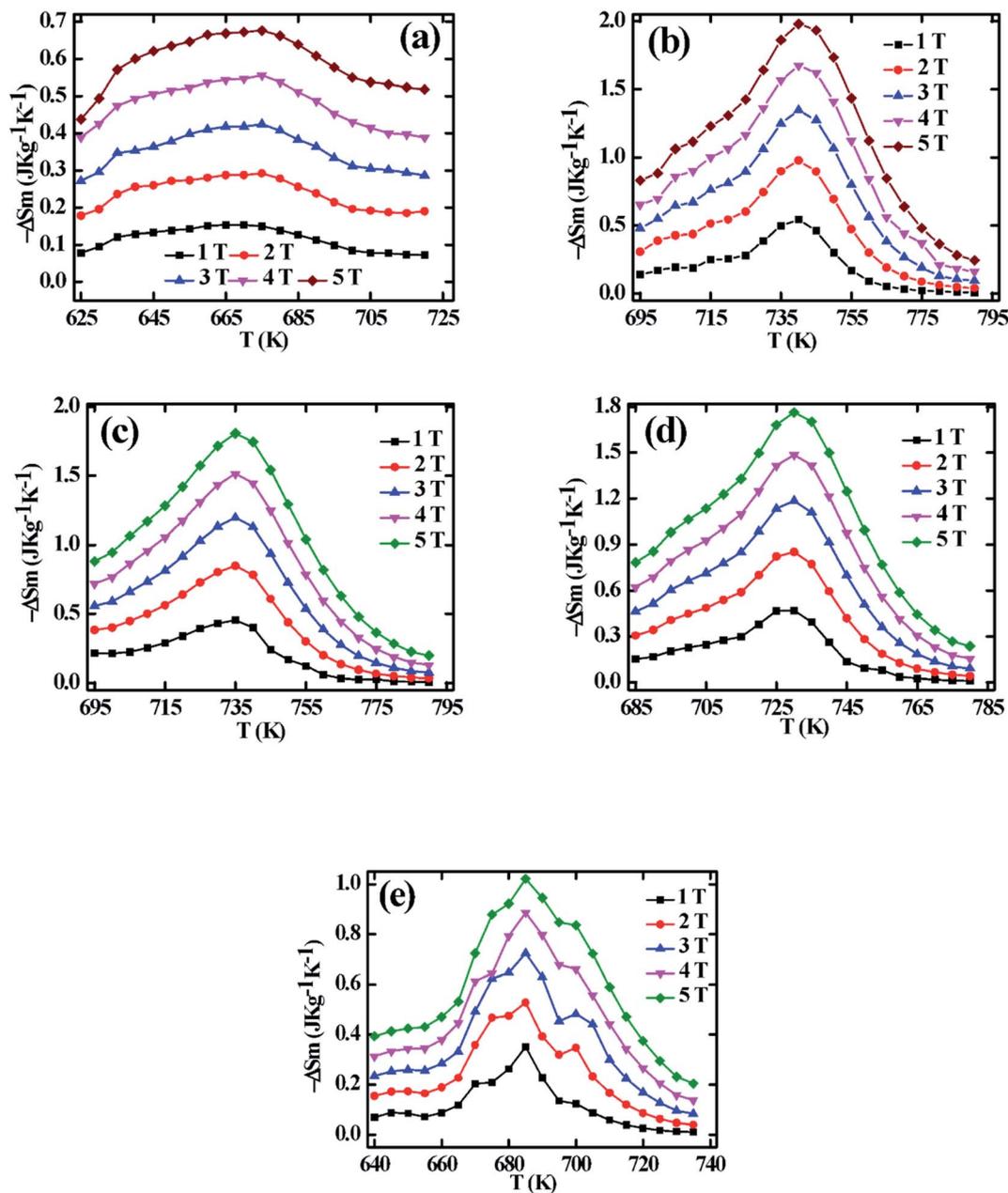


Fig. 10 Magnetic entropy change as a function of temperature for various  $\text{Co}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ . (a)  $x = 0.0$ , (b)  $x = 0.125$ , (c) 0.25, (d) 0.375, and (e)  $x = 0.500$ .

Table 3 Comparison of the Curie temperature,  $|\Delta S_m^{\max}|$  and RCP for various  $\text{Co}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$  and some other reported samples

Samples	$T_C$ (K)	$\mu_0 H$ (T)	$ \Delta S_m^{\max} $ $\text{J kg}^{-1} \text{K}^{-1}$	RCP ( $\text{J kg}^{-1}$ )	Reference
$\text{CoFe}_2\text{O}_4$	675	5	0.66	35.7	This work
$\text{Co}_{0.875}\text{Cr}_{0.125}\text{Fe}_2\text{O}_4$	740	5	1.98	128	
$\text{Co}_{0.75}\text{Cr}_{0.25}\text{Fe}_2\text{O}_4$	735	5	1.8	137	
$\text{Co}_{0.625}\text{Cr}_{0.375}\text{Fe}_2\text{O}_4$	731	5	1.76	145	
$\text{Co}_{0.5}\text{Cr}_{0.5}\text{Fe}_2\text{O}_4$	687	5	1.02	52	
$\text{Ni}_{0.6}\text{Cd}_{0.2}\text{Cu}_{0.2}\text{Fe}_2\text{O}_4$	680	5	2.12	125	Ref. 4
$\text{Zn}_{0.4}\text{Ni}_{0.2}\text{Cu}_{0.4}\text{Fe}_2\text{O}_4$	565	5	1.41	141	Ref. 29
$\text{Ni}_{0.4}\text{Mg}_{0.3}\text{Cu}_{0.3}\text{Fe}_2\text{O}_4$	690	5	1.56	136	Ref. 30
$\text{Zn}_{0.25}\text{Ni}_{0.25}\text{Mg}_{0.5}\text{Fe}_2\text{O}_4$	590	5	1.16	90	Ref. 31
$\text{Mg}_{0.6}\text{Cu}_{0.2}\text{Ni}_{0.2}\text{Fe}_2\text{O}_4$	670	5	1.38	137	Ref. 32
$\text{Mg}_{0.6}\text{Cu}_{0.4}\text{Fe}_2\text{O}_4$	630	5	1.09	136	Ref. 32



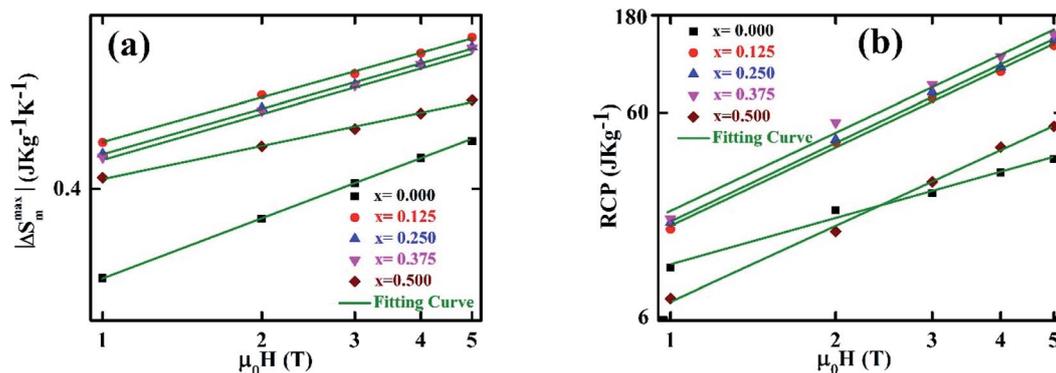


Fig. 11 Magnetic field dependence (a)  $|\Delta S_m^{\max}|$  at  $T_C$  fitted to the power law  $|\Delta S_m^{\max}| \propto (\mu_0 H)^\gamma$ , (b) RCP at  $T_C$  fitted to the power law  $\text{RCP} \propto (\mu_0 H)^{1+1/\delta}$ .

**3.3.2 Kouvel–Fisher plot.** The  $\beta$ ,  $\gamma$ , and  $T_C$  have been calculated from the Kouvel–Fisher plots (KFPs) that provide more reliable values.<sup>47</sup> In KFPs  $\beta$ ,  $\gamma$ , and  $T_C$  has been extracted from  $M_{\text{SP}} \left[ \frac{dM_{\text{SP}}}{dT} \right]^{-1}$  and  $\chi_0^{-1} \left[ \frac{d\chi_0^{-1}(T)}{dT} \right]^{-1}$  vs.  $T$  graph (Fig. 8) according to the following expressions:<sup>34</sup>

$$M_{\text{SP}} \left[ \frac{dM_{\text{SP}}}{dT} \right]^{-1} = \frac{T - T_C}{\beta} \quad (19)$$

$$\chi_0^{-1} \left[ \frac{d\chi_0^{-1}}{dT} \right]^{-1} = \frac{T - T_C}{\gamma} \quad (20)$$

$T_C$  values are extracted from the X-intercepts, and critical  $\beta$  and  $\gamma$  values are obtained from the inverse of slopes of the fitted straight line of Fig. 8. The estimated  $\beta$ ,  $\gamma$ , and  $T_C$  values for all the samples according to KFPs are tabulated in Table 2, where  $\beta$ ,  $\gamma$ , and  $T_C$  values are well-matched with the values as the mean-field theory for  $x = 0.125, 0.250,$  and  $0.375$ . However, for  $x = 0.00$ , and  $0.500$  the  $\beta$ , and  $\gamma$  values calculated from KFPs show a remarkable difference compared to that of mean-field theory.

To ensure the reliability of  $\beta$ ,  $\gamma$ , and  $T_C$  values another robust method have been elucidated by plotting  $M|\varepsilon|^{-\beta}$  vs.  $\mu_0 H|\varepsilon|^{-(\beta+\gamma)}$  just above and below  $T_C$  according to eqn (17). The  $M|\varepsilon|^{-\beta}$  vs.  $\mu_0 H|\varepsilon|^{-(\beta+\gamma)}$  have been plotted for all samples in Fig. 9. The inset in Fig. 9, each case displays the same data plotted on a log-log scale. From Fig. 9, it is evident that two separate groups of isotherms superimpose (one group greater than  $T_C$ , and the other group less than  $T_C$ ) for the samples  $x = 0.125, 0.250,$  and  $0.375$ . These results suggest the accuracy of  $\beta$ ,  $\gamma$ , and  $T_C$  values from which it can be decided that these three compositions ( $x = 0.125, 0.250,$  and  $0.375$ ) are a universal class of material. From the inset of Fig. 9, two branches (one below  $T_C$  and other above  $T_C$ ) show the linear behavior in the high field region while in the low field region show some deviation from linearity. These behaviors confirm that the scale theory gives more important data in higher fields. The isotherms for  $x = 0.00$ , and  $0.500$  show different behavior that imply the non-universal class of the materials.

### 3.4 Magnetocaloric effect

The MCE properties is an intrinsic properties of magnetic materials that can be calculated by calculating the magnetic entropy change ( $\Delta S_m$ ) around  $T_C$ . The  $\Delta S_m$  values are calculated from the isothermal M–H data based on Maxwell's thermodynamic relation:<sup>34</sup>

$$\Delta S_m = \int \frac{dM}{dT} dH \quad (21)$$

The calculated  $\Delta S_m$  for all samples show negative values for all temperature and applied magnetic field. The calculated  $-\Delta S_m$  values as a function of temperature are illustrated in Fig. 10 for all samples at different magnetic fields up to 5 T. From Fig. 10, the peak values of  $-\Delta S_m$  are defined as maximum entropy change  $|\Delta S_m^{\max}|$  are evident at  $T_C$  or close to  $T_C$ . From Fig. 10 it is observed that  $|\Delta S_m^{\max}|$  increases with an increase of magnetic field are due to the spin ordering for all the samples. The  $|\Delta S_m^{\max}|$  values are tabulated in Table 3 for 5 T for all samples. Table 3 shows that for  $x = 0.125$ , maximum entropy change is observed, however, a decreasing trend is found for further increasing of Cr content. The similar behavior is observed for  $M_s$ .

Relative Cooling Power (RCP) is another important criterion that helps to characterize the MCE of such magnetic materials. The RCP for all samples has been calculated using the following relation:<sup>4</sup>

$$\text{RCP} = |\Delta S_m^{\max}| \times \delta T_{\text{FWHM}} \quad (22)$$

where  $\delta T_{\text{FWHM}}$  is the full width of the  $0.5|\Delta S_m^{\max}|$ . The calculated RCP values are tabulated in Table 3, where very lower values of RCP with lower  $|\Delta S_m^{\max}|$  for  $x = 0.00$  are evident which may be due to the non-universal nature as explained in Section 3.3. For  $x = 0.125, 0.250,$  and  $0.375$  it show the comparable values of RCP reported earlier for various ferrite materials.<sup>4,29–32</sup> From Table 3, RCP values are found to increase with the increasing Cr content and found a maximum of  $145 \text{ J kg}^{-1}$  for  $x = 0.375$  which is higher than the previously reported RCP values.<sup>4,29–32</sup> For  $x = 0.500$  the RCP values are found to be very low which may be due



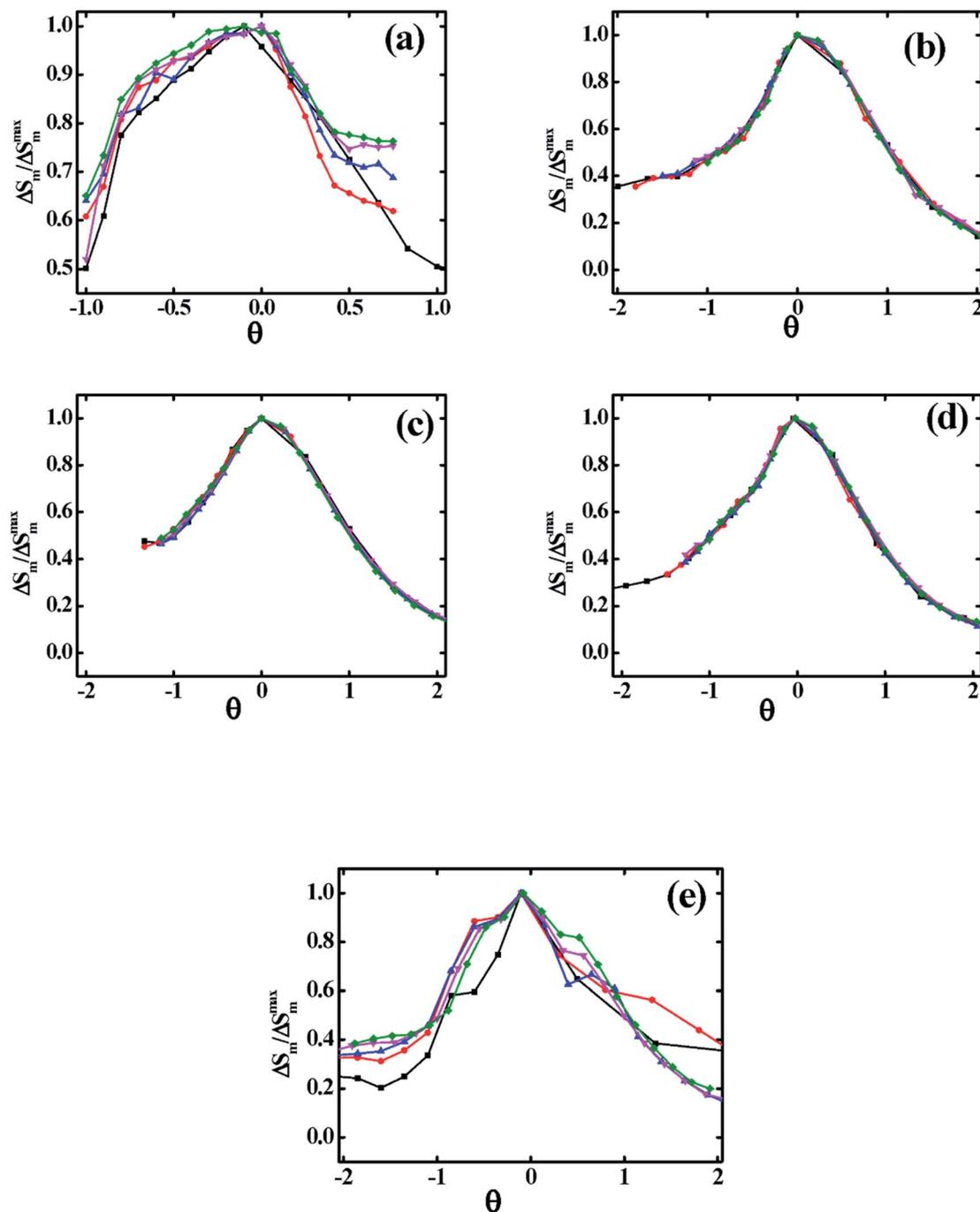


Fig. 12 Normalized magnetic entropy change as function of rescaled temperature for various  $\text{Co}_{1-x}\text{Cr}_x\text{Fe}_x\text{Fe}_2\text{O}_4$ . (a)  $x = 0.0$ , (b)  $x = 0.125$ , (c) 0.25, (d) 0.375, and (e)  $x = 0.500$ .

to showing negative values of the vacancy parameter as explained in the previously reported article.<sup>25</sup> Another reason behind showing the lower values of RCP is non-universal behavior for  $x = 0.500$ .

To analyze the critical exponent, the magnetic field dependent  $|\Delta S_m^{\max}|$  and RCP are fitted according to the following power law:<sup>38</sup>

$$|\Delta S_m^{\max}| \propto (\mu_0 H)^n \quad (23)$$

$$\text{RCP} \propto (\mu_0 H)^{1+\frac{1}{n}} \quad (24)$$

where,  $n$  is the exponent that depends on the magnetic state of the samples. The  $|\Delta S_m^{\max}|$  vs.  $\mu_0 H$  are plotted in the log-log scale and illustrated in Fig. 11(a) for all samples, and the values of  $n$  are obtained from the slope of the linear fitting. The obtained  $n$  values have been tabulated in Table 2. To explain the reliability of this exponent, calculated the value of  $n$  at/near  $T_C$  by using the following relation:<sup>34</sup>



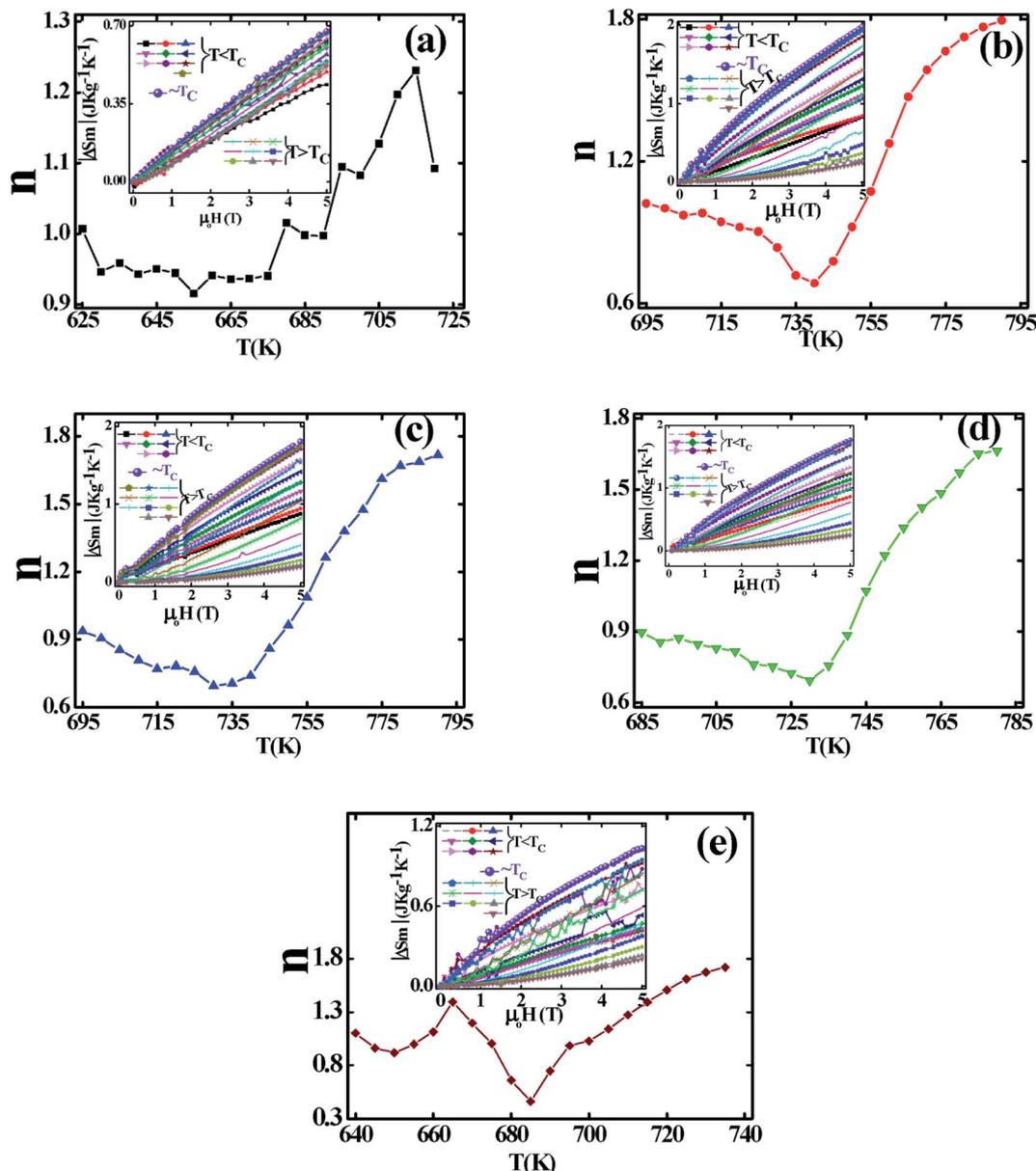


Fig. 13 The exponent  $n$  as function of temperature obtained from the fitting of field dependent isothermal magnetic entropy change at various temperature for various  $\text{Co}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$ . (a)  $x = 0.0$ , (b)  $x = 0.125$ , (c)  $0.25$ , (d)  $0.375$ , and (e)  $x = 0.500$ .

$$n = 1 + \frac{\beta - 1}{\beta + \gamma} \quad (25)$$

By applying the Widom relation eqn (18) and (25) can be rewritten as

$$n = 1 + \frac{1}{\delta} \left( 1 - \frac{1}{\beta} \right) \quad (26)$$

The calculated  $n$  exponents (using eqn (26)) have been tabulated in Table 2 for all compositions. In this case  $\beta$  and  $\gamma$  values are considered from KFPs, and values of  $\delta$  are considered from the critical isotherms. The exponent calculated from eqn

(26) are in good agreement with those obtained from the fitted curve of Fig. 11(a) for  $x = 0.125$ ,  $0.250$ , and  $0.375$ . For  $x = 0.00$ , and  $0.500$ , there is a large difference in the value of  $n$ .

The  $\delta$  values have been obtained from the slope of the linear fit of the RCP vs.  $\mu_0H$  plot in the log-log scale (Fig. 11(b)) according to eqn (24). The obtained  $\delta$  values by this method are tabulated in Table 2, from where  $\delta$  values show a good agreement with those of  $\delta$  values obtained from Widom scaling and critical isotherms for the samples  $x = 0.125$ ,  $0.25$ , and  $0.375$  (Sec. 3.3). However, for  $x = 0.00$ ,  $0.500$  a large difference of  $\delta$  values has been obtained. Comparing the values of  $n$  and  $\delta$  according to Fig. 11, and critical scaling it is decided that the MCE properties of present compositions are reliable.



Verification of critical phenomena and the nature of the magnetic phase transition of these materials are also important. In 2006, Franco *et al.* have utilized the phenomenological universal scaling curve.<sup>39</sup> According to this method normalized magnetic entropy as a function of re-scaled temperature  $\theta$  (eqn (27)) has been plotted at several magnetic fields which are depicted in Fig. 12.

$$\theta = \begin{cases} -\frac{T - T_C}{T_{r1} - T_C}, & T \leq T_C \\ \frac{T - T_C}{T_{r2} - T_C}, & T \geq T_C \end{cases} \quad (27)$$

where,  $T_{r1}$  and  $T_{r2}$  are two-temperatures corresponding to  $0.5|\Delta S_m^{\max}|$ .

In Fig. 12(b-d) it is observed that the results of various magnetic field collapsed into a single master curve, which implies that synthesized samples of  $x = 0.125, 0.250$ , and  $0.375$  are in universal class and show exact second-order phase transition.<sup>34</sup> However, from Fig. 12(a and e) it is evident that for  $x = 0.00$ , and  $0.500$ , samples are non-universal class.

To analyze the accuracy of MCE properties and order of phase transition, the value of  $n$  is calculated using the following expression:<sup>38</sup>

$$n(T, \mu_0 H) = \frac{d \ln |\Delta S_m|}{d \ln \mu_0 H} \quad (28)$$

The calculated  $n$  values as a function of  $T$  are illustrated in Fig. 13 for all samples where the inset depicted the  $|\Delta S_m|$  vs.  $\mu_0 H$ . From the Fig. 13(b-d), it is found that the  $n$  values for  $x = 0.125, 0.250, 0.375$  are close to 1 below  $T_C$  which suggests that the  $dM/dT$  term in eqn (21) is weakly field-dependent.<sup>34</sup> With an increase in temperature it is observed the decreasing trend and arrive the minimum  $n$  values of 0.684, 0.695, and 0.693 at  $T_C$  for  $x = 0.125, 0.25$ , and  $0.375$ , respectively. These  $n$  values are consistent with the  $n$  values obtained from Fig. 11(a) and also from eqn (26) as tabulated in Table 2. Above  $T_C$ , the  $n$  values are found to be the increasing trend but do not cross the critical value of 2 for  $x = 0.125, 0.250$ , and  $0.375$ . The minimum  $n$  values at  $T_C$  and  $n < 2$  above  $T_C$  confirm the second-order phase transition which is explained by Law *et al.*<sup>38</sup> For  $x = 0.00$ , and  $0.500$  as evident from Fig. 13(a and e) it is found the anomalous behavior of  $n$ - $T$  curves shows the minimum  $n$  values at  $T_C$  which is very different compared with that of the  $n$  values described in Sec. 3.3. This behavior for  $x = 0.00$ , and  $0.500$  is non-universal class of materials showing the non-realistic MCE values. Although  $n$ - $T$  shows anomalous behavior, however,  $n$  values less than 2 for all the temperature suggest that the samples ( $x = 0.00$ , and  $0.500$ ) exhibit the second-order phase transition.

## 4 Conclusions

The effect of  $\text{Cr}^{3+}$  substitution on the magnetic and MCE properties of various  $\text{Co}_{1-x}\text{Cr}_x\text{Fe}_2\text{O}_4$  prepared by the solid-state reaction technique have been evident in this report. The Arrott plot from the analysis of M-H isotherms exhibits the second-order phase transition that has been perfectly confirmed from

the critical analysis and scaling analysis of the MCE effect. The  $x = 0.125, 0.250$ , and  $0.375$  samples demonstrate high RCP values in the range of 127–145  $\text{J kg}^{-1}$  compared to that of other ferrites. The universal curve scaling and scaling analysis of the MCE effect confirms the universal class and the MCE values for  $x = 0.125, 0.250$ , and  $0.375$  are reliable. The higher MCE values up to 145  $\text{J kg}^{-1}$  are observed for  $x = 0.375$ , which might be considered as potential candidates for the cooling technology. On the other hand, the higher microwave frequency for all compositions makes them a strong candidate for high-frequency microwave applications, especially in satellite communications and biomedical applications.

## Conflicts of interest

There are no conflicts to declare.

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