



Magnetoelastic and giant frequency dispersion in MnCo_2O_4 spinel: Quenched Jahn-Teller distortion by Cr and Fe substitution

A.D. Singha^a, P. Pramanik^b, M. Reehuis^c, D.M. Többsen^c, T. Sarkar^b, R. Athira^{d,e}, S.D. Kaushik^d, R. Mathieu^b, S. Thota^{a,*}

^a Department of Physics, Indian Institute of Technology Guwahati, Assam 781039, India

^b Department of Materials Science and Engineering, Uppsala University, SE-75103, Sweden

^c Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, Berlin D-14109, Germany

^d UGC-DAE Consortium for Scientific Research, Mumbai Centre, 246-C CFB, BARC, Trombay, Mumbai 400085, India

^e Savitribai Phule Pune University, Ganeshkhind, Pune, Maharashtra, 411007, India

ARTICLE INFO

Keywords:

Ferrimagnetism
Spinel
Neutron diffraction
Jahn-Teller distortion
Magnetoelastic features
Frequency dispersion

ABSTRACT

We report magnetoelastic (0.46%) features and giant frequency dispersion ($\Delta\omega \sim 317$ rad/s, $\Delta T \sim 34$ K) of ac-magnetic susceptibility ($\chi_{ac}(\omega, T)$) at two distinct temperatures ($T_{P1-ac} = 144$ K and $T_{P2-ac} = 211$ K) in Cr and Fe co-substituted MnCo_2O_4 cubic ($Fd\bar{3}m$) spinel forming the composition $\text{Cr}_{0.2}\text{Mn}_{0.8}\text{Fe}_{0.4}\text{Co}_{1.6}\text{O}_4$. A detailed temperature dependence of neutron and synchrotron x-ray diffraction studies reveal anomalous changes in the lattice parameter across ferrimagnetic (FiM) ordering ($T_C = 260$ K), as well as at two additional transitions $T_{S1} \sim 114$ K and $T_{S2} \sim 173$ K. Competing antiferromagnetic exchange interactions among the cations ($J_{AA}/k_B = 23.2$ K, $J_{BB}/k_B = 9.15$ K, and $J_{AB}/k_B = 25.25$ K) are responsible for the giant frequency dispersion observed in $\chi_{ac}(\omega, T)$, while ruling out the presence of a conventional spin-glass state below T_C . The Kubelka Munk analysis of the optical absorbance data is used to find the optical band gap of 1.16 eV (E_g). The optical absorption spectrum reveals well defined $d-d$ transitions attributed to the charge transfer in this investigated system. Such substantial red-shift compared to the pristine p -type semiconducting Co_3O_4 together with the FiM behavior of this compound may open a constructive approach for applications in magneto electronics.

1. Introduction

Conflicting interatomic forces at low temperatures, quantum fluctuations, competing exchange interactions and atomic disorder/dilution plays a crucial role in stabilizing the ground state of any magnetic system which may also decide the degeneracy present in their low-energy state [1–5]. Such scenario commonly results in frustration either in terms of geometric aspects or in terms of their magnetic/spin arrangement, where in the former case spin-orbit coupling and magneto-crystalline anisotropy contributes synergistically [2–4]. Consequently, many interesting phenomena arise in those compounds which exhibit very high degree of magnetic frustration. As examples spin-liquid and spin-glass behavior, unconventional quantum singularities, giant bipolar exchange-bias effect and magnetoelastic/magnetoelectric features etc., [6–8]. Usually, complex oxides comprising of the transition metal (TM) oxides exhibit above specified unconventional magnetic features [9–12].

Among strongly correlated electronic systems exhibiting the features described above, insulating and semiconducting spinel oxides ($AB_2\text{O}_4$) occupy an important place in the scientific literature [9–12]. In particular, the electronic structure of TM elements such as Co and Mn at tetrahedral (A) or octahedral (B) sites gives rise to a wide variety of magnetodielectric and magnetoelastic/structural properties, which are of interest for applications in magnetoelectronics and transformer cores [10]. Substitution of non-magnetic elements at TM sites further introduces intriguing magnetic behavior, characterized by competing ferromagnetic (FM) and antiferromagnetic (AFM) interactions. Such systems can exhibit zero net magnetization while maintaining finite spin-polarized electronic bands at the Fermi level. Elements such as Sn, Ti and Zn play a key role when incorporated in Co_3O_4 based spinels which usually show a disorder driven reentrant spin-glass state with weaker AFM or ferrimagnetic (FiM) interactions [13–15]. On the contrary, the nonmagnetic Zn substitution at the Co site in SnCo_2O_4 diminishes the glassy phase and favors long-range FM order, but beyond a

* Corresponding author.

E-mail address: subhasht@iitg.ac.in (S. Thota).

<https://doi.org/10.1016/j.jalcom.2026.187534>

Received 31 December 2025; Received in revised form 19 February 2026; Accepted 21 March 2026

Available online 22 March 2026

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percolation limit of 50% substitution at Co sites the AFM-FM interaction regenerates the glassy characteristics [15]. However, in the case of high T_C compound CoFe_2O_4 (CFO), the anisotropy associated with Co^{2+} ions drive the spin relaxation to exhibit a glassy state [16]. Rare-earth elements substitution in CFO causes enhanced spin-glass transition temperature along with interesting changes in crystal symmetry which are coupled through exchange interactions between $4f$ and $3d$ electrons [17]. Similarly, Co-implanted rutile- TiO_2 single crystals exhibit superparamagnetic (SPM) behavior characterized by a low blocking temperature, highlighting the role of Co-induced spin centers and their orbital interactions with the host lattice [18]. These findings emphasize the significant influence of spin-orbit coupling on the magnetic relaxation dynamics observed in Co-based oxide systems. The emergence of SPM features and nanocluster formation within the lattice is not solely attributed to the nanoscale confinement of spin domains, but also to the interplay between local spin interactions and the anisotropy energy barrier, even in systems with bulk-like grain sizes. In general, the exchange interactions between Co^{2+} ions and their surrounding atomic environment favor the stabilization of long-range magnetic order in polycrystalline bulk grain size compounds. However, the introduction of structural or chemical disorder can significantly weaken these exchange interactions, leading to the breakdown of long-range order. As a result, the system transits toward short-range magnetic ordering, often manifesting as SPM behavior or the formation of nanoscale magnetic clusters [19]. Also, in spinel oxides, the presence of strong spin-orbit coupling further complicates the magnetic relaxation behavior, introducing additional anisotropy and influencing the dynamics of spin fluctuations and cluster formation. Divalent Co ions, possessing partially unquenched orbital-angular momentum, impart significant magnetocrystalline anisotropy, thereby increasing the energy barrier for magnetic moment reversal and contributing to the emergence of unconventional glassy magnetic behavior [20]. The local atomic environment including the spin-relaxation process is also very susceptible to the cationic substitution, precise lattice distortions, temperature, and micro-strain present in the compound.

On the other hand, magnetoelastic phenomena arising from magnetostriction modify the local orbital states of divalent Co ions, thereby altering the anisotropy landscape [20]. Such interactions and couplings account for the emergence of temperature-sensitive lattice anomalies as well as the pronounced frequency dispersion observed in the ac susceptibility. Notably, among the Cr-based spinels, MnCr_2O_4 compound exhibit anomalies in the lattice parameter across the spin-spiral state, a direct manifestation of magnetoelastic effects, whereas CoCr_2O_4 exhibits ferroelectricity driven by the magnetoelastic effect [21,22]. Co-based rare-earth double perovskites, such as SmSrCoFeO_6 , exhibit anisotropic lattice expansion associated with ferrimagnetic ordering, which enhances the magnetocaloric response [23]. This entanglement of magnetic characteristics and magnetoelasticity in Co-based oxides highlights their potential as promising candidates for strain-controlled spintronic devices, low-power magnetic switches, and tunable susceptibility in actuators and sensors [24].

Motivated by the above-discussed features of frustrated magnets, in the present work we have chosen MnCo_2O_4 (MCO) as the base compound. This system provides a platform to investigate spin-orbital interactions through site-specific substitution of TM elements, which in turn modifies both the relaxation dynamics and crystal symmetry [25–28]. Furthermore, MCO exhibits anomalous hysteresis behavior below the ordering temperature, wherein the anisotropy field exceeds the coercivity (H_C) [29].

Such unusual magnetic responses, together with the non-stoichiometry ($\text{MCO}_{4+\delta}$), lead to significant modifications in the electrical resistivity, magnetic structure including the exchange interactions [29,30]. When reduced to the nanoscale, MCO based compounds exhibit more disorder in them and giant frequency dispersion in ac-magnetic susceptibility appears as an essential feature [27,28,31]. A 50% Ru substitution in MCO results in a pronounced colossal

magnetoresistance around 80 K, whereas complete replacement of Mn by Ru drives the system into a glassy state near 16 K [32]. Neutron diffraction measurements on Ti containing MCO reveal interactive Jahn-Teller (JT) distortions in the BO_6 octahedra, which become increasingly evident with higher Mn concentration [25]. These compounds display a compensation point near 25 K along with weak spin-glass behavior around 110 K [25]. Furthermore, site-specific substitution of Ti and Fe in MCO induces structural distortions coupled with cluster-glass behavior, underscoring the interplay between competing magnetic interactions and tetragonal distortions [27]. In addition to these intriguing magnetic phenomena, MCO and its derivatives have also been extensively investigated for applications in supercapacitors [33], fuel cells [34,35], water splitting [36], and catalysis [37].

In this study, we present a comprehensive investigation of the structural and magnetic behavior of Cr- and Fe-substituted MCO bulk polycrystals with the ratio 1: 2. Synchrotron x-ray diffraction together with neutron diffraction analyses of the investigated system reveal pronounced magnetoelastic coupling. These structural anomalies emerge concurrently with the onset of FiM ordering temperatures, accompanied by anomalous variations in the frequency dispersion of the ac-magnetic susceptibility. Such correlations provide direct evidence for the formation of unusual SPM nanoclusters, driven by magnetoelastic anomalies. With increasing Cr/Fe content, the magnetoelastic features are enhanced, enabling stronger spin-lattice coupling. The investigated system further modifies the anisotropy energy landscape, thereby inducing giant frequency-dependent magnetic relaxation.

2. Experimental methodology

Polycrystalline bulk samples of $\text{Cr}_{0.2}\text{Mn}_{0.8}\text{Fe}_{0.4}\text{Co}_{1.6}\text{O}_4$ (hereafter denoted as Cr_2Fe_4 for brevity) were synthesized by the conventional solid-state reaction method using stoichiometric amounts of binary transition-metal oxides MnO_2 , Co_3O_4 , Cr_2O_3 , and Fe_2O_3 as raw materials. These oxides were thoroughly mixed in an agate mortar with pestle for 5 h in air to ensure homogeneity, followed by pelletization into 13 mm disks under an applied load of 50 kN using stainless steel KBr die set. The pellets were subsequently sintered in air at 1200°C for 8 h with a heating rate of $4^\circ\text{C}/\text{min}$, and then cooled to room temperature. Phase purity of the synthesized compound was confirmed by laboratory powder x-ray diffraction (XRD) using a high-resolution Rigaku diffractometer which operates with $\text{Cu-K}\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$). Additionally, temperature-dependent (from 25 to 295 K) synchrotron powder x-ray diffraction measurements were performed at the KMC-2 beamline of BESSY II, Helmholtz-Zentrum Berlin, Germany, operated with a wavelength of $1.14947(10) \text{ \AA}$ [38]. This beamline is equipped with a modified Gifford-McMahon closed-cycle cryocooler TMP-CCR HXR [39]. All x-ray powder data as well as the neutron powder data, considered further below, were analyzed by Rietveld refinement using the *FullProf* suite [40]. The results of the Rietveld refinements of the synchrotron powder patterns recorded at 25, 260 and 295 K are presented in figure S1 of the Supplementary Information part (SI). The crystal and magnetic structures were further investigated by neutron powder diffraction, carried out at the high-resolution neutron powder diffractometer PD-III at the Dhruva reactor of Bhabha Atomic Research Centre (BARC) in Trombay, developed by the UGC-DAE CSR Mumbai Centre. This instrument is equipped with a multi-position sensitive detector (PSD) and a double bent perfect Si monochromator selecting the neutron wavelength $\lambda = 1.48 \text{ \AA}$.

Elemental composition and valence states were probed by high-resolution x-ray photoelectron spectroscopy (XPS) on a PHI 5000 VersaProbe III system (Physical Electronics, USA) equipped with a monochromatic $\text{Cu-K}\alpha_1$ source. Magnetic measurements were performed using a Quantum Design Physical Property Measurement System (PPMS). Temperature- and field-dependent dc magnetization (M - T and M - H) were recorded in the range from 2 to 300 K under field up to $\pm 90 \text{ kOe}$. Additional high-temperature magnetization measurements

were carried out on a second PPMS system (Quantum Design), capable of extending measurements up to 400 K. Furthermore, *ac*-magnetic susceptibility was measured using a Quantum Design Magnetic Property Measurement System (SQUID-MPMS XL-5) to obtain dynamic magnetic responses. To probe the optical bandgap of the system, we performed the absorption measurement in the ultra-violet, visible and near-infrared region ($\lambda_{\text{opt}} = 250 - 860$ nm) by means of spectrophotometer from Perkin Elmer (model: Lambda-950). These measurements are performed under diffuse reflectance mode.

3. Results and analysis

3.1. Crystal and magnetic structure

To investigate the crystal structure of Cr₂Fe₄ a combined synchrotron and neutron powder diffraction study was carried out on the high-intensity synchrotron beamline KMC-2. The analysis of x-ray diffraction data of nominal Cr₂Fe₄ revealed that this compound exhibits the highest possible symmetric cubic structure with the space group $Fd\bar{3}m$ down to 25 K, where the lattice constant is $a = 8.3360(9)$ Å obtained at 290 K. Compared to the value $a = 8.2859(5)$ Å of Mn_{1.17}Co_{1.85}O₄ it is 0.60% larger [26]. The crystallite size $d \sim 2.6$ µm of Cr₂Fe₄ was obtained using the histogram analysis of log-normal analysis using field emission scanning electron microscopy (FESEM) images of Cr₂Fe₄ (figure S2 of SI). More information on the cation distribution was achieved from Rietveld refinements of the neutron powder data collected at 290 K as shown in Fig. 1. Here it is important to note that the neutron scattering lengths of the different metal atoms ($b_{\text{Cr}} = 0.3635$ fm, $b_{\text{Mn}} = -0.373$ fm, $b_{\text{Fe}} = 0.945$ fm and $b_{\text{Co}} = 0.249$ fm) strongly differ, hence emphasis has been given on the negative value of Mn. The refinements were again carried out in the space group $Fd\bar{3}m$ resulting in a residual $R_F = \sum ||F_{\text{obs}}| - |F_{\text{calc}}|| / \sum |F_{\text{obs}}| = 0.0281$. Since A site is practically fully occupied with Co atoms in slightly different composition Cr_{0.1}Mn_{0.9}Fe_{0.2}Co_{1.8}O₄, for the current case

only a minor Fe content of 0.7% was found to be located at the A site giving the formula (Co_{0.993}Fe_{0.007})_A[Cr_{0.10}Mn_{0.90}Fe_{0.193}Co_{0.807}]_BO₄ [28]. Accordingly, we refined the occupancy of the Co atoms at the A sites, where a slightly enlarged value of $\text{occ}(\text{Co}_A) = 1.067(10)$ was obtained. This indicates that only Fe can partially replace Co atoms at this site, since it is having the strongest neutron scattering length. Finally, it was found that the A site contains 97.5(4)% Co and 2.5(4)% Fe giving the following cationic distribution (Co_{0.975(4)}Fe_{0.025(4)})_A [Cr_{0.20}Mn_{0.80}Fe_{0.375(4)}Co_{0.625(4)}]_BO₄. This trend can be confirmed for the other Fe richer compounds Ti_{0.20}Mn_{0.80}Fe_{0.36}Co_{1.64}O₄ and Ti_{0.40}Mn_{0.60}Fe_{0.87}Co_{1.13}O₄, where the Co atoms at the A site are replaced by 5.5(5) and 17.3(4) % Fe, respectively [27].

Due to the fact, that the neutron scattering length of the lightest O atom ($b_O = 5.803$ fm) gives a relatively stronger scattering power than in x-ray diffraction, the A-O- and B-O-bond lengths could be determined with better accuracy. In the AO₄ tetrahedron, in our case (Co_{0.975}Fe_{0.025})_AO₄, one obtains the bond length $d(\text{A-O}) = 1.9706(3)$ Å which is similar to the value $d(\text{A-O}) = 1.9737(3)$ Å found recently in the isostructural compound (Co_{0.993}Fe_{0.007})_A[Cr_{0.10}Mn_{0.90}Fe_{0.193}Co_{0.807}]_BO₄ [28]. However, this value is slightly smaller in comparison to the value $d(\text{Co}_A\text{-O}) = 1.967(3)$ Å for Mn_{1.15}Co_{1.85}O₄ system [26] as well as the calculated bond length of 1.96 Å using the ionic radii listed by Shannon [41]. Accordingly, the bond length $d(\text{B-O}) = 1.9929(3)$ Å in the BO₆ octahedron of Cr₂Fe₄ is found to be similar to $d(\text{B-O}) = 1.9941(3)$ Å determined recently for Cr_{0.10}Mn_{0.90}Fe_{0.2}Co_{1.8}O₄ [28]. These values are slightly larger than the B-O bond length, $d(\text{B-O}) = 1.977(3)$ Å, previously reported for off-stoichiometric Mn_{1.15}Co_{1.85}O₄, or more specifically, (Co)_A[Mn_{1.15}Co_{0.85}]_BO₄ [26]. Interestingly, the observed values are significantly smaller than 2.046, 2.044 and 2.054 Å calculated for Cr_{0.10}Mn_{0.90}Fe_{0.20}Co_{1.8}O₄, Cr_{0.20}Mn_{0.80}Fe_{0.40}Co_{1.60}O₄ and Mn_{1.15}Co_{1.85}O₄, respectively. These bond lengths support the fact that the Co³⁺ ions in both compounds are in the low-spin state. Assuming a high-spin state of Co³⁺ the calculated bond lengths in both compounds would increase up to 2.08 Å.

The temperature dependence of the cubic lattice parameter a for the Cr₂Fe₄ system was determined between 25 and 295 K using the KMC-2 beamline. Fig. 2(a) shows anomalies in the a vs. T curve at the Curie temperature ($T_C = 260$ K), as well as at $T_{S1} = 114$ K and $T_{S2} = 173$ K within the magnetically ordered regime, reflecting the onset of magnetoelastic effects. The most significant change occurs at T_{S2} , where $\Delta a = 0.00186(7)$ Å. Since no lowering of the space-group symmetry was detected, a spontaneous shift of a T-O bond length should induce a change in the lattice parameter a along either the [100] or [111] directions. Notably, the four $d(\text{A-O})$ bonds of the AO₄ tetrahedra are oriented along [1 1 1], [1 1 1], [1 1 1], and [1 1 1], while the six $d(\text{B-O})$ bonds of the BO₆ octahedra point along [100], [010], and [001] directions (and their opposites). Practically no change is observed for the B-O bond lengths, with $d(\text{B-O}) = 1.9917(5)$ Å at 150 K and 1.9914(5) Å at 230 K. In contrast, a significant decrease in $d(\text{A-O})$ is found from 230 to 150 K, changing from 1.9695(5) Å to 1.9649(5) Å, corresponding to $\Delta d(\text{A-O}) = 0.0046(5)$ Å. Given that the B-O bonds lie along [111], the associated shift along [100] is $\Delta a/\sqrt{3} = 0.0027(3)$ Å. These results provide clear evidence that the magnetoelastic effects in this system are localized exclusively within the AO₄ tetrahedra.

The magnetic structure of Cr₂Fe₄ was investigated in detail to probe its ground state using neutron powder diffraction (NPD) data collected at 3 K. Fig. 1 presents the neutron powder patterns of Cr₂Fe₄ recorded at 3 and 290 K. The crystal structure was refined in the cubic space group $Fd\bar{3}m$. Due to ferrimagnetic coupling between the A and B sublattices, strong magnetic intensity appears at the positions of the nuclear reflections 111, where the nuclear contribution is weak. No magnetic intensity is found at the position of the reflection 200 which is forbidden in the used space group. The calculated patterns (blue solid line) between observed ones (black circles). The difference patterns (blue solid line) between observed and calculated intensities are also shown as well as the positions of nuclear (N) and magnetic (M) Bragg reflections. An additional reflection is observed around $2\theta \sim 43^\circ$ in the powder pattern collected at 3 K. Our data analysis revealed that this reflection does not belong to the investigated spinel or another impurity. We assume that a small part of the cryostat partially scatters in the neutron beam due to thermal dilatation.

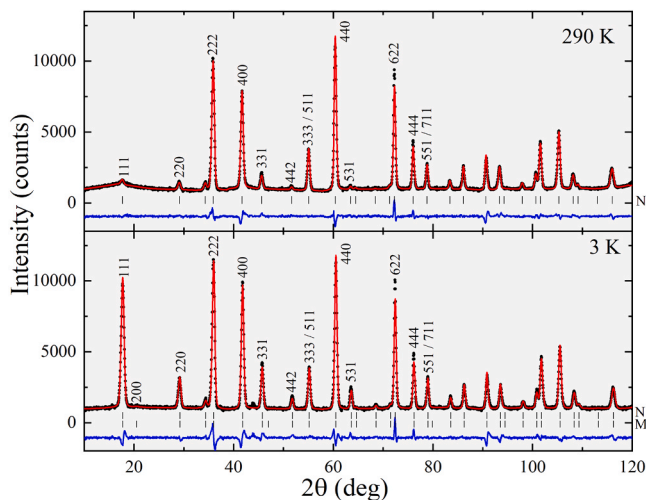


Fig. 1. Neutron powder patterns of Cr₂Fe₄ collected at 3 and 290 K. The crystal structure was refined in the cubic space group $Fd\bar{3}m$. Due to the ferrimagnetic coupling between the A and B sublattices strong magnetic intensity appears at the position of the nuclear reflection 111, where the nuclear contribution is weak. No magnetic intensity is found at the position of the reflection 200 which is forbidden in the used space group. The calculated patterns are compared with the observed ones (black circles). The difference patterns (blue solid line) between observed and calculated intensities are also shown as well as the positions of nuclear (N) and magnetic (M) Bragg reflections. An additional reflection is observed around $2\theta \sim 43^\circ$ in the powder pattern collected at 3 K. Our data analysis revealed that this reflection does not belong to the investigated spinel or another impurity. We assume that a small part of the cryostat partially scatters in the neutron beam due to thermal dilatation.

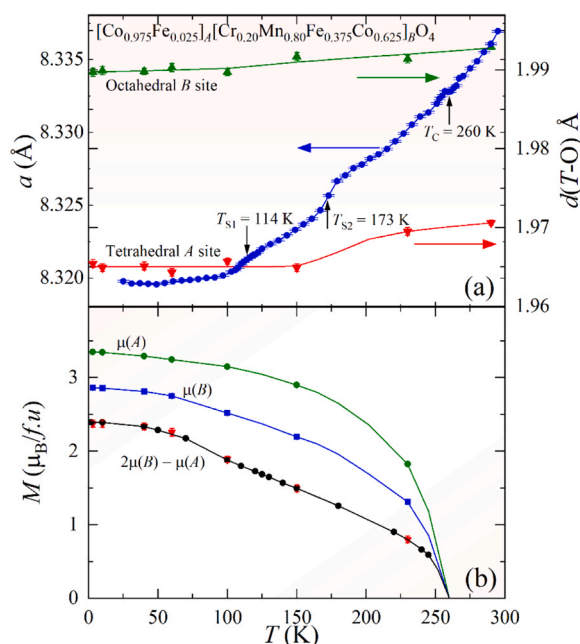


Fig. 2. Results of the Rietveld refinements of Cr₂Fe₄. The distribution of the transition metals T at the tetragonal A and octahedral B site is $A = \text{Co}_{0.975}\text{Fe}_{0.025}$ and $B = \text{Cr}_{0.20}\text{Mn}_{0.80}\text{Fe}_{0.375}\text{Co}_{0.625}$, respectively. (a) Thermal variation of the cubic lattice parameter a and the $d(T-O)$ bond lengths. Synchrotron powder data revealed anomalies in the a vs. T curve at the Curie temperature T_C , as well as in the magnetically ordered range at T_{S1} and T_{S2} due to the onset of magnetoelastic effects. A significant anomaly could only be found for the bond lengths $d(A-O)$ as determined from neutron powder data. (b) Thermal variation of the magnetic moments of the transition metal atoms at the tetrahedral A and octahedral B sites. The resulting ferromagnetic moment $2\mu(B) - \mu(A)$ represents the spontaneous magnetization M_S obtained from PPMS measurements. This has been used as a constraint to refine the individual magnetic moments of the A and B sites with good accuracy using our neutron powder data. The lines connecting the data points are visual guides.

confirms a similar ferrimagnetic ground state, although its Curie temperature $T_C = 260$ K is higher. To determine the individual magnetic moments at the A and B sites, the constraint $M_S = 2\mu(T_B) - \mu(T_A)$ was applied. The resulting ferromagnetic moment corresponds to the spontaneous magnetization M_S , as determined from PPMS measurements, indicated by black filled circles and a guiding black line in Fig. 2(b). The refined ferrimagnetically coupled magnetic moments are $\mu_F(T_A) = 3.35(2) \mu_B$ and $\mu_F(T_B) = 2.86(2) \mu_B$ using the $M_S = 2\mu(T_B) - \mu(T_A) = 2.38(3) \mu_B$. For comparison, the earlier study on $\text{Cr}_{0.10}\text{Mn}_{0.90}\text{Fe}_{0.2}\text{Co}_{1.8}\text{O}_4$ reported $M_S = 2\mu(T_B) - \mu(T_A) = 1.80(3) \mu_B$, $\mu_F(T_A) = 3.41(2) \mu_B$ and $\mu_F(T_B) = 2.60(2) \mu_B$ [28]. Similar values of A -site magnetic moments were obtained for both compounds, consistent with nearly full occupancy by Co^{2+} ions.

In contrast to $\text{Cr}_{0.10}\text{Mn}_{0.90}\text{Fe}_{0.2}\text{Co}_{1.8}\text{O}_4$, approximately 2.5% of Co^{2+} is replaced by Fe^{2+} at the A site in Cr₂Fe₄. To compare the magnitudes of the magnetic moments, the spin-only values, $\mu_S = gS \mu_B$, of the transition-metal ions were considered. The ordered Co^{2+} moment would reach $\mu(\text{Co}^{2+})_A = 3 \mu_B$, which is larger than the experimentally obtained values. The spin-only moment of Fe^{2+} , $\mu(\text{Fe}^{2+})_A = 4 \mu_B$, would further increase the total moment; however, its contribution is expected to be negligible due to the low concentration. It is also possible that both Mn^{2+} and Fe^{2+} substitute Co^{2+} at the A site, where their negative and positive neutron scattering lengths may partially compensate each other. A better agreement between calculated and experimental moments was previously found for $\text{Mn}_{1.15}\text{Co}_{1.85}\text{O}_4$, where the observed moment of $3.1 \mu_B$ is only slightly larger, consistent with the A site being occupied exclusively by Co atoms [26].

In the next step, we estimated the individual magnetic moments of Cr^{3+} , Mn^{3+} , and Fe^{3+} , according to the cationic distribution $(\text{Co}_{0.975}\text{Fe}_{0.025})_A [\text{Cr}_{0.20}\text{Mn}_{0.80}\text{Fe}_{0.375}\text{Co}_{0.625}]_B \text{O}_4$. It is well known that Co^{3+} ions adopt a low-spin state due to the large crystal-field splitting of the $3d$ orbitals, such that their magnetic moment is expected to be negligible. For the refinement, we used the constraint $\mu(\text{Fe}^{3+})_B = 0.8 \times \mu(\text{Mn}^{3+})_B = 0.6 \mu(\text{Cr}^{3+})_B$, assuming high-spin states with the spin-only values $\mu(\text{Cr}^{3+})_B = 3 \mu_B$, $\mu(\text{Mn}^{3+})_B = 4 \mu_B$, and $\mu(\text{Fe}^{3+})_B = 5 \mu_B$. For Cr₂Fe₄, the refined moments were: $\mu(\text{Cr}^{3+})_B = 3.01(3) \mu_B$, $\mu(\text{Mn}^{3+})_B = 4.01(4) \mu_B$, $\mu(\text{Fe}^{3+})_B = 5.17(5) \mu_B$. These values are comparable to those obtained earlier for $\text{Cr}_{0.10}\text{Mn}_{0.90}\text{Fe}_{0.2}\text{Co}_{1.8}\text{O}_4$ [28], namely $\mu(\text{Cr}^{3+})_B = 3.14(3) \mu_B$, $\mu(\text{Mn}^{3+})_B = 4.19(5) \mu_B$, $\mu(\text{Fe}^{3+})_B = 5.23(3) \mu_B$, although in both compounds the refinements yield slightly enhanced values compared to the spin-only estimates. To estimate the magnitude of the trivalent Co moment, we fixed the Mn^{3+} moment to $3.84 \mu_B$, as reported for the pristine system MCO [42], again using the constraint $\mu(\text{Fe}^{3+})_B = 0.8 \times \mu(\text{Mn}^{3+})_B = 0.6 \mu(\text{Cr}^{3+})_B$. The resulting value, $\mu(\text{Co}^{3+})_B = 0.61(9) \mu_B$ is very similar to the Co moment obtained for $\text{Cr}_{0.10}\text{Mn}_{0.90}\text{Fe}_{0.2}\text{Co}_{1.8}\text{O}_4$ [28], $\mu(\text{Co}^{3+})_B = 0.59(7) \mu_B$. A comparable trend has also been reported for $\text{Ti}_{0.60}\text{Mn}_{0.40}\text{Co}_2\text{O}_4$ and $\text{Ti}_{0.80}\text{Mn}_{0.20}\text{Co}_2\text{O}_4$ [25], where the B -site Co^{3+} ions carry a small moment in the range 0.6 – $0.8 \mu_B$. In this study, the fixed value $\mu(\text{Mn}^{3+})_B = 3.84 \mu_B$ from Ref. [42] was also used.

Furthermore, it is noteworthy that the B -site moment $\mu_F(T_B) = 2.60(2) \mu_B$ in $\text{Cr}_{0.10}\text{Mn}_{0.90}\text{Fe}_{0.2}\text{Co}_{1.8}\text{O}_4$ is slightly smaller than $\mu_F(T_B) = 2.86(2) \mu_B$ in the Cr₂Fe₄ compound. To estimate the theoretical B -site moments, we considered the spin-only values $\mu(\text{Cr}^{3+})_B = 3 \mu_B$, $\mu(\text{Mn}^{3+})_B = 4 \mu_B$, and $\mu(\text{Fe}^{3+})_B = 5 \mu_B$. In addition, for both compounds we used the experimentally determined magnetic moment $\mu(\text{Co}^{3+})_B = 0.6 \mu_B$. For Cr₂Fe₄, the calculated moment is: $\mu_S(T_B^{3+}) = [0.20 \mu(\text{Cr}^{3+})_B \times 0.80 \mu(\text{Mn}^{3+})_B \times 0.375 \mu(\text{Fe}^{3+})_B \times 0.625 \mu(\text{Co}^{3+})_B] / 2 = 3.03 \mu_B$. For $\text{Cr}_{0.10}\text{Mn}_{0.90}\text{Fe}_{0.2}\text{Co}_{1.8}\text{O}_4$, the corresponding value is: $\mu_S(T_B^{3+}) = [0.10 \mu(\text{Cr}^{3+})_B \times 0.90 \mu(\text{Mn}^{3+})_B \times 0.193 \mu(\text{Fe}^{3+})_B \times 0.807 \mu(\text{Co}^{3+})_B] / 2 = 2.67 \mu_B$. These calculated spin-only moments show good agreement with the experimentally refined values discussed above.

3.2. Elemental analysis

The possible oxidation states of the constituent elements in Cr₂Fe₄ were investigated in detail by x-ray photoelectron spectroscopy (XPS). Fig. 3 depicts the core-level binding energy spectra for (a) Mn-2p, (b) Cr-2p, (c) Co-2p, (d) Fe-2p, and O-1s. For precise analysis, all spectra were calibrated using the C-1s reference peak at 284.8 eV. Background subtraction was performed using the Tougaard function in XPSPEAK41, and the core-level peaks were fitted with Gaussian-Lorentzian line shapes. The Mn-2p spectrum (Fig. 3(a)) deconvolutes into three principal peaks: M_1 at ~641.1 eV (Mn-2p_{3/2}) and M_2 at ~653.1 eV (Mn-2p_{1/2}), corresponding to Mn^{3+} states, and M_3 at ~643.9 eV (Mn-2p_{3/2}), associated with Mn^{4+} . A broad satellite peak (S_{M1}) is observed at ~663.2 eV [43]. The energy separation between the doublet (Mn-2p_{1/2} – Mn-2p_{3/2} ~ 12 eV) further confirms the presence of Mn^{3+} [43]. A similar splitting has been reported for $\text{Mn}_{0.6}\text{Ti}_{0.4}\text{Co}_{1.2}\text{Fe}_{0.8}\text{O}_4$ [27], confirming the dominant trivalent Mn state. The higher intensity of the Mn^{3+} peak compared to Mn^{4+} indicates a reduced concentration of Mn^{4+} . Such mixed $\text{Mn}^{3+}/\text{Mn}^{4+}$ valence states, also observed in MCO are known to facilitate hole hopping ($\text{Mn}^{3+} \leftrightarrow \text{Mn}^{4+}$), which contributes to unusual $M-H$ hysteresis behaviour via domain wall pinning. The Cr-2p spectrum (Fig. 3(b)) is deconvoluted into three peaks: C_1 (~576 eV, Cr-2p_{3/2}), C_2 (~584.8 eV, Cr-2p_{1/2}), and C_3 (~587 eV). All lie within the standard binding energy ranges reported in the NIST database [44]. The doublet separation ($C_2 - C_1 \sim 8.8$ eV) is characteristic of trivalent Cr [45].

The Co-2p spectrum (Fig. 3(c)) reveals six features, comprising two pairs of spin-orbit doublets and two satellites. The first doublet, with P_1 (~779.4 eV) and P_2 (~794.5 eV), corresponds to Co^{3+} ($\Delta E \sim 15.1$ eV). The second doublet, with P_3 (~780.3 eV) and P_4 (~796.2 eV), corresponds to Co^{2+} ($\Delta E \sim 15.9$ eV) [46,47]. In addition, two satellite peaks

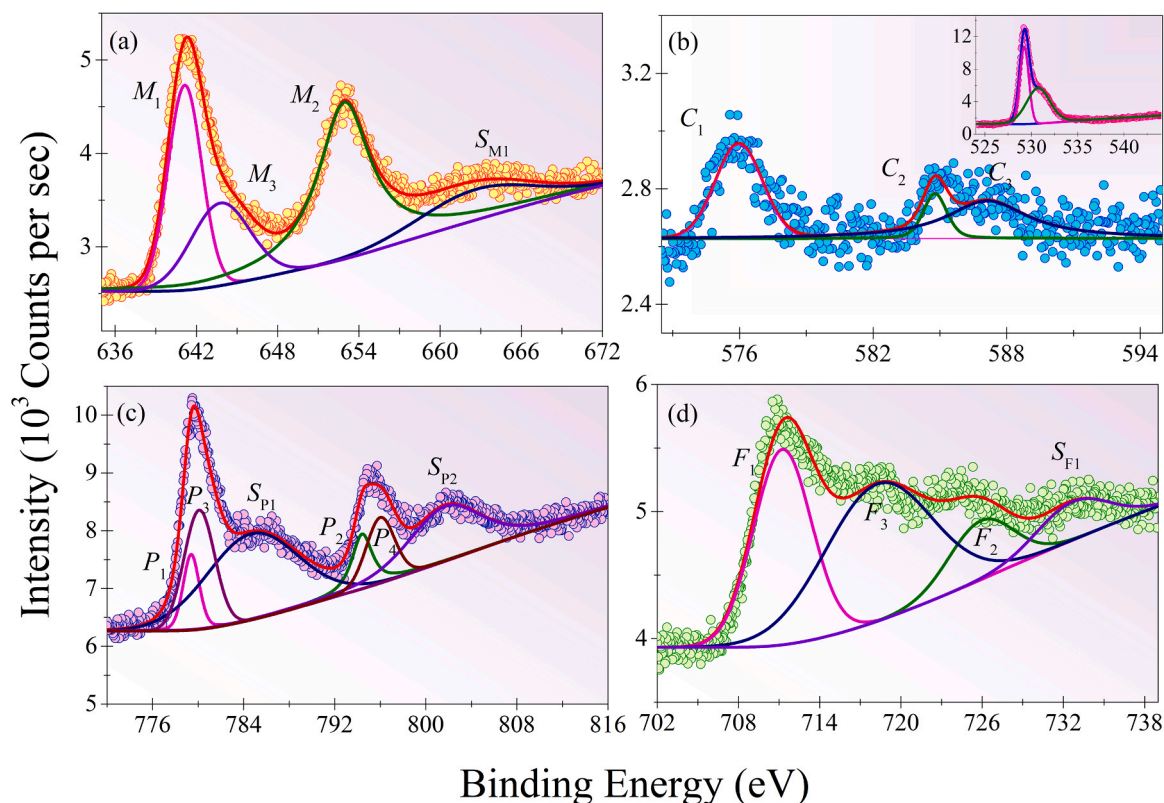


Fig.-3. The core level x-ray photoelectron spectrum of: (a) Mn-2p, (b) Cr-2p, (c) Co-2p, (d) Fe-2p and O-1s (inset in b) that are present in Cr2Fe4 compound.

($S_{P1} \sim 785.2$ eV and $S_{P2} \sim 802.2$ eV) are observed, which generally perceived by the compounds prevailing divalent Co state [47].

The Fe-2p spectrum (Fig. 3(d)) exhibits a complex structure deconvoluted into three principal peaks: F_1 at ~ 711.0 eV (Fe-2p_{3/2}) and F_2 at ~ 726.1 eV (Fe-2p_{1/2}), with a spin-orbit splitting of $\Delta E \sim 15.1$ eV, characteristic of Fe³⁺ at the octahedral site [48,49]. An additional feature at F_3 (~ 718.5 eV) indicates the presence of Fe²⁺, while a satellite peak at S_{F1} (~ 732.8 eV) further supports mixed-valence Fe [49]. The O-1s spectrum (inset of Fig. 3(b)) contains two components. The intense peak at ~ 529.2 eV corresponds to lattice oxygen (Mn–O, Cr–O, Co–O, Fe–O bonds) in Cr2Fe4 [50,51]. A broad shoulder at ~ 530.7 eV is attributed to surface-absorbed oxygen species [52].

4. Variation of magnetization and magnetic susceptibility

4.1. Temperature dependence

The temperature dependence of magnetization, $M(T)$, for Cr2Fe4 was measured under zero-field-cooled (ZFC) and field-cooled (FC) protocols in the temperature range from 3 to 300 K with an applied dc field of $H_{DC} = 500$ Oe (Fig. 4(a)). In ZFC protocol, the sample was initially cooled to 3 K without an applied magnetic field from the paramagnetic (PM) state, and the magnetization was recorded during warming cycle. Whereas in FC protocol the sample was cooled under the same conditions but with an applied magnetic field and data were collected during warming cycle.

As shown in Fig. 4(a) $M_{ZFC}(T)$ increases upon cooling, exhibits a

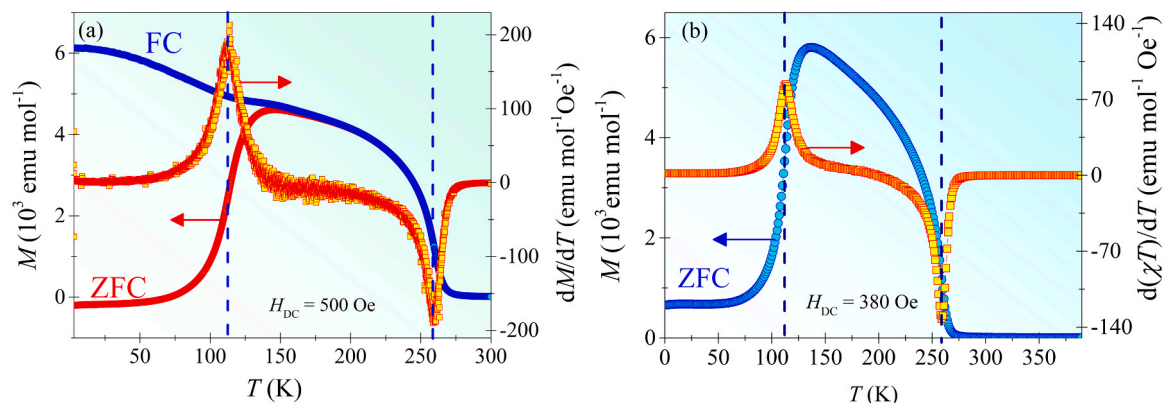


Fig. 4. (a) Left hand scale presents the temperature dependence of the magnetization (M) of the Cr2Fe4 compound measured with $H_{DC} \sim 500$ Oe dc magnetic field for both zero-field-cooled (ZFC) and field-cooled (FC) modes. The right-hand scale shows the temperature variation of dM/dT for ZFC mode, here the minimum at $T_C \sim 260$ K represents the ferrimagnetic ordering temperature. (b) Left hand scale presents the temperature dependence (2 – 390 K) of M of the same Cr2Fe4 compound as measured in $H_{DC} \sim 380$ Oe only for the ZFC mode as shown in left hand scale. Here the minimum using $d(M/T)/dT$ vs. T variation for ZFC curve data as shown in the right-hand scale also represents $T_C \sim 260$ K.

broad maximum near 140 K and decreases steadily at lower temperatures. A clear bifurcation between $M_{FC}(T)$ and $M_{ZFC}(T)$ occurs at the irreversible temperature $T_{irr} \sim 210$ K, below which the two curves diverge, reflecting strong irreversibility arising from moment anisotropy. At higher temperatures, a negative transition is observed at ~ 260 K in the derivative curve dM/dT vs. T (right axis of Fig. 4(a)), corresponding to the ferrimagnetic ordering temperature (T_C) from the PM state. Notably, the $M_{FC}(T)$ data show a wavy feature around ~ 110 K, coinciding with a distinct positive peak in dM/dT , suggesting the presence of a locally unstable magnetic state.

Additional ZFC magnetization measurements were performed on the same sample using a Quantum Design PPMS in the wider temperature range from 2 to 390 K with $H_{DC} = 380$ Oe to examine the high-temperature PM region. The corresponding ZFC magnetisation $M(T)$ and the first derivative of magnetic susceptibility $\chi_{ZFC}(T) (= M/H)$ are shown in Fig. 4(b). The transition features identified are consistent with those obtained under $H_{DC} = 500$ Oe, confirming the robustness of the observed ferrimagnetic transition at $T_C \sim 260$ K.

For comparison, the pristine compound MCO exhibits a lower T_C , ranging from ~ 140 K (nanocrystalline phase) to ~ 180 K (bulk polycrystalline) [29,53]. In MCO, the cationic distribution $(Co^{2+})_A[Mn^{3+}Co^{3+}]_BO_4$ gives rise to dominant Co_A - Mn_B -superexchange interactions via oxygen. In contrast, substitution of Cr and Fe in Cr2Fe4 favours localization of Fe^{3+} and Cr^{3+} at the B site, thereby strengthening B-B superexchange interactions and enhancing the ferrimagnetic ordering temperature to ~ 260 K.

To gain deeper insight into the exchange interactions of Cr2Fe4, the temperature dependence of inverse paramagnetic susceptibility was analyzed using Néel's molecular-field theory for a two-sublattice model [54,55]. The expression is given by

$$\frac{1}{\chi_A} = \frac{T}{C} + \frac{1}{\chi_N} - \left[\frac{\sigma_0}{T - \theta} \right] \quad (1)$$

Here, the first two terms resemble the Curie-Weiss law forming a hyperbolic asymptote, while the last term accounts for the characteristic hyperbolic divergence near the ferrimagnetic (FiM) transition. For analysis, the dc magnetic susceptibility was corrected by subtracting the temperature-independent Hartree-Fock susceptibility, i.e., $\chi_A^{-1} = (\chi - \chi_D)^{-1}$, where $\chi_D \sim -0.000131054$ emu mol⁻¹ Oe⁻¹ represents the diamagnetic contribution of all atoms. The corrected susceptibility was then inverted as $\chi_A^{-1} = (\chi - \chi_D)^{-1}$ and fitted to Eq. (1) in the paramagnetic (PM) region above T_C .

The best fit (blue solid line in Fig. 5) yielded the parameters: Weiss

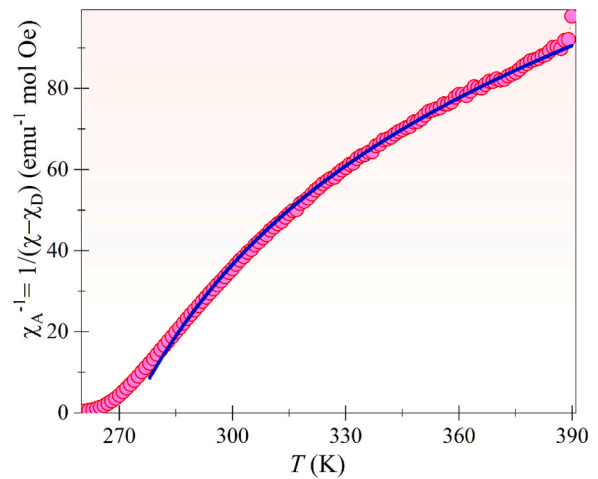


Fig. 5. The temperature dependence of the inverse paramagnetic susceptibility $\chi_A^{-1}(\chi_A = \chi - \chi_D)$ of the Cr2Fe4 compound, here the solid line represents the best fit to the Néel Eq. (1). Here, $\chi_D = -1.3 \times 10^{-4}$ emu mol⁻¹ Oe⁻¹ represents the Hartree-Fock diamagnetic susceptibility for the Cr2Fe4 compound.

Cr_{0.1}Mn_{0.9}Fe_{0.2}Co_{0.8}O₄ reported recently indicating that the super exchange interaction is enhanced with increasing the Cr/Fe concentration. In case of its pristine MCO one finds $\mu_{eff} \sim 7.92$ μ_B /f.u., 8.1 μ_B /f.u. for their domain size $d \sim 42$ nm and 471 nm, respectively. Whereas for $d \sim 8$ nm the moment μ_{eff} decreases to 7.16 μ_B /f.u., usually noticed in nanostructures due to the surface atomic disorder and finite size effects. With a minute substitution of Cu in MCO (i.e., MnCo_{1.8}Cu_{0.2}O₄) the moment μ_{eff} decreases slightly to 7.51 μ_B /f.u. While substituting with highly-magnetic Ti and Fe at Mn and Co sites, respectively, it leads to a reduction of μ_{eff} to 4.32 μ_B /f.u. [27]. Further we employed the Néel model for ferrimagnetism, specifically for the two-sublattices and determined the molecular field constants following the mathematical description given below in Eqs. (2 - 4) [55]:

$$\frac{1}{\chi_N} = \frac{1}{C^2} (C_A^2 N_{AA} + C_B^2 N_{BB} + 2C_A C_B N_{AB}) \quad (2)$$

$$\theta = \frac{C_A C_B}{C} (2N_{AB} - N_{AA} - N_{BB}) \quad (3)$$

$$\sigma_0 = \frac{C_A C_B}{C^3} \{ C_A^2 (N_{AA} - N_{AB})^2 + C_B^2 (N_{BB} - N_{AB})^2 - 2C_A C_B [N_{AB}^2 - (N_{AA} + N_{BB})N_{AB} + N_{AA}N_{BB}] \} \quad (4)$$

temperature $\theta = 205$ K, $\sigma_0 = 7710.6$ mol Oe K emu⁻¹, $\chi_N = 0.0144$ emu mol⁻¹ Oe⁻¹, and Curie constant $C = 6.2$ emu K mol⁻¹ Oe⁻¹. The asymptotic Curie temperature was estimated as $T_a = \frac{C}{\chi_N} \sim 430.6$ K, which reflects the strength of antiferromagnetic (AFM) interactions between A-B sublattices [56]. For Cr2Fe4, the ratio $T_a/T_C \sim 1.87 > 1$ indicates intrinsic magnetic frustration [57]. Using the relation $C = \frac{N_A \mu_{eff}^2}{3k_B}$ the effective magnetic moment was obtained as $\mu_{eff} \sim 7.04$ μ_B per formula unit (f.u.). This experimental value is in close agreement with the calculated $\mu_{eff} \sim 6.96$ μ_B /f.u., derived from the cationic distribution $(Co_{0.9}^{2+}Fe_{0.1}^{2+})_A[Cr_{0.20}^{3+}Mn_{0.80}^{3+}Fe_{0.5}^{3+}Co_{0.7}^{3+}]_BO_4$ and the spin-only contributions of Co^{2+} (3.87 μ_B), Fe^{2+} (4.90 μ_B), Cr^{3+} (3.87 μ_B), Mn^{3+} (4.90 μ_B), Fe^{3+} (5.90 μ_B), and Co^{3+} (0 μ_B). The effective magnetic moment of the investigated compound Cr2Fe4 is about $\mu_{eff} \sim 6.96$ μ_B /f.u. which is slightly larger in comparison to ~ 6.5 μ_B /f.u. of its sister compound

$$T_C = -\frac{1}{2} (C_A N_{AA} - C_B N_{BB}) + \frac{1}{2} \{ (C_A N_{AA} - C_B N_{BB})^2 + 4C_A C_B N_{AB}^2 \}^{1/2} \quad (5)$$

The values C_A and C_B are proportional to g_A^2 and g_B^2 , respectively. Solving these equations yielded molecular field constants $N_{AA} = 102.61$, $N_{BB} = 4.16$, and $N_{AB} = 128.48$. Substituting these values into Eq. (5) gives $T_C \sim 273$ K, in good agreement with the experimental value ($T_C = 260$ K). Finally, the exchange interaction constants were estimated as $J_{AA}/k_B = 23.2$ K, $J_{BB}/k_B = 9.15$ K, and $J_{AB}/k_B = 25.25$ K. The hierarchy $J_{AB} > J_{AA}$, J_{BB} is characteristic of spinel systems [58] and confirms the dominant AFM coupling between A and B sublattices in Cr2Fe4. If we compare the above magnitudes with the pristine MCO of $d \sim 471$ nm in

its bulk gives smaller $J_{AB}/k_B \sim 11$ K yet keeping the same trend ($J_{AB} > J_{AA}$) in which case $J_{BB}/k_B = 9$ K and $J_{AA}/k_B = 7.75$ K. However, reducing the domain size to 42 nm, the interaction pattern modifies as $J_{BB} > J_{AB} > J_{AA}$ [59]. In this case the antiferromagnetic exchange constants $J_{BB}/k_B = 21.24$ K, $J_{AA}/k_B = 8.4$ K and $J_{AB} = 13.9$ K indicate that the octahedral (*B-B*) exchange interactions dominate at nanoscale. A similar dominance of *B-B* interactions is also followed by the polycrystalline Mn_3O_4 compound as: $J_{BB}/k_B = 19.9$ K, $J_{AA}/k_B = 4.9$ K, and $J_{AB}/k_B = 6.8$ K [56].

4.2. Dynamical susceptibility: frequency and field dependence

To probe the origin of the magnetic transitions observed in dc magnetization, we performed frequency- and dc field-dependent ac magnetic susceptibility ($\chi_{ac} = \chi'_{ac} + \chi''_{ac}$) measurements in the temperature range from 100 to 280 K under frequency spanning range between 0.51 and 510 Hz (Δf), with an applied ac driving field $h_{ac} = 4$ Oe. The frequency dependence of the real $\chi'(f, T)$ and imaginary $\chi''(f, T)$ components for Cr2Fe4 are presented in Fig. 6(a) and (b), respectively. No additional transitions were detected outside this temperature range. Within the measured window Δf , both $\chi'(f, T)$ and $\chi''(f, T)$ exhibit three distinct transition regimes, which we classify as: region I (100 – 180 K), region II (180 – 235 K), and region III (above 235 K).

Region III exhibits a sharp, intense peak in both χ' and χ'' without any frequency dispersion, suggesting long-range ferrimagnetic transition at $T_C \sim 260$ K. However, a clear frequency dispersion is evident in regions I and II, most prominently in $\chi''(f, T)$. As seen in Fig. 6(c, d) the dynamical response of the system is rapidly changed upon application of a bias dc field. The peaks in $\chi''(f, T)$ are essentially suppressed in a bias field of 50 Oe in regions II and III, while they survive up to a bias of 500 Oe in region I.

The peaks observed in region I are relatively broad and reminiscent of superparamagnetic nanoparticles or clusters [60,61]. To quantify the frequency dispersion in regions I ($\Delta\omega_1 \sim 317$ rad/s, $\Delta T_{P1-ac} \sim 35$ K), we used the Mydosh parameter $\Omega = \frac{\Delta T_p}{T_{p1}(\log_{10} f_2 - \log_{10} f_1)}$, where $\Delta T_p \sim (T_{p2} - T_{p1})$ is the difference between peak temperatures corresponding to frequencies f_2 and f_1 . Generally, $\Omega > 10^{-2}$ indicates a SPM or nanocluster phase, whereas $\Omega < 10^{-2}$ is associated with spin-glass behaviour

[62–67]. For Cr2Fe4, $\Omega \sim 0.12$ in region I (T_{P1-ac}), which is consistent with the superparamagnetic behaviour of magnetic clusters.

The temperature and frequency dependence of $\chi''(f, T)$ in region II (T_{P2-ac}) is different. The peaks in that region are barely defined in low frequencies, but “grow” in magnitude with increasing frequency (see Fig. 6b). Their frequency shifts are however minimal. This behaviour suggests dynamical magnetic behaviour akin to that observed in magnetically frustrated systems, which may show non-linearities in a probing magnetic field (or here ac excitation) [64]. However, a detailed empirical scaling law analysis (pertaining to both Power-law of critical scaling down (PLCSD) and Vogel-Fulcher law (VFL) reveals that the peak maxima of T_{P1-ac} and T_{P2-ac} in $\chi_{ac}(f, T)$ does not follow the scaling laws. All the relevant data obtained from the mathematical fits of PLCSD and VFL are given in the supplementary data (see figure S3 and S4).

Neutron diffraction shows well-defined magnetic reflections, without diffuse scattering. Hence the magnetometry results suggest that the ferrimagnetic phase established in region III is either magnetically frustrated, or built up of magnetic clusters, possibly owing to the presence of nonmagnetic Co^{3+} ions at the *B* site, which disrupt the magnetic network. In the first case, the magnetic frustration yields the dynamical effects observed in region II and leaves out small non-interacting clusters, coexisting with the long-ranged ordered phase; the blocking of these clusters giving rise to the superparamagnetic relaxation observed in region I [61]. Another possibility is that it is the magnetic ordering of the individual clusters which is observed in region III; those clusters do not interact and exhibit the superparamagnetic relaxation observed in region I. As in the other scenario, the relaxation in region II is associated with magnetic frustration of the ferrimagnetic phase established in region III; here within each magnetic cluster. This may also account for the similar dc bias fragility of the dynamics in regions II and III, in comparison to the more robust region I (Fig. 6c, d).

4.3. Field dependent and critical behavior

The magnetization hysteresis loops $M(T)$ vs. H recorded at 4, 120, and 160 K up to an applied field of 50 kOe are shown in Fig. 7(a - c). Saturation occurs within 20 kOe, consistent with ferromagnetic (FM) ordering of the intrinsic magnetization. At low temperatures, strong

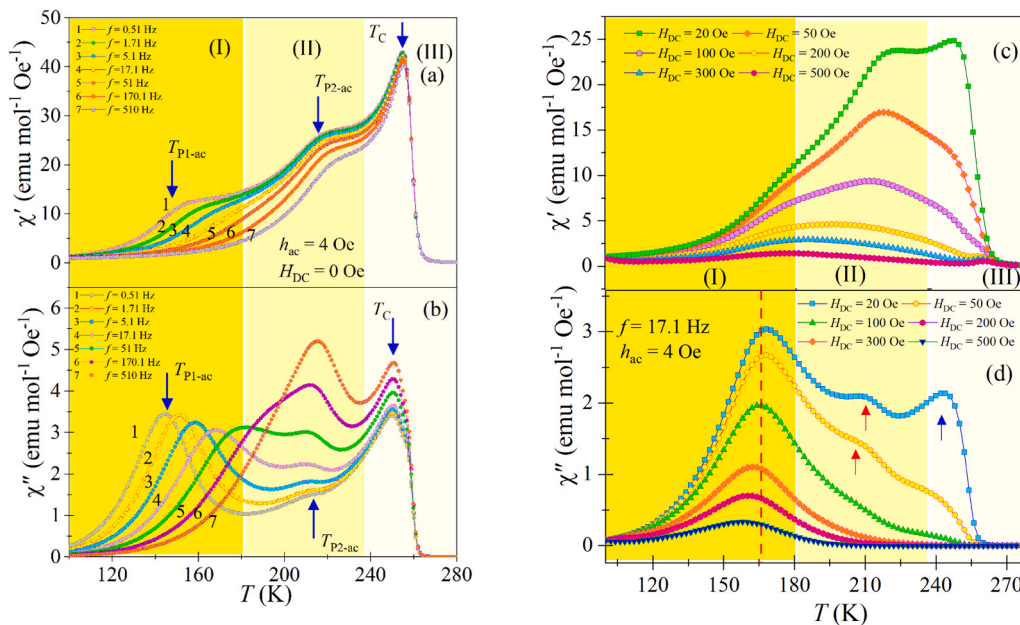


Fig. 6. (a, b) Temperature dependence of the in phase $\chi'(f, T)$ and out-of-phase ac magnetic susceptibilities, $\chi''(f, T)$ of the Cr2Fe4 compound as measured for several frequencies $f = 0.17 - 510$ Hz with $H_{DC} = 0$ Oe and $h_{ac} = 4$ Oe. (c, d) Temperature variation of $\chi'(f, T)$ and $\chi''(f, T)$ of Cr2Fe4 measured for various dc magnetic fields $H_{DC} = 20 - 500$ Oe, with $h_{ac} = 4$ Oe at a fixed frequency $f = 17.1$ Hz.

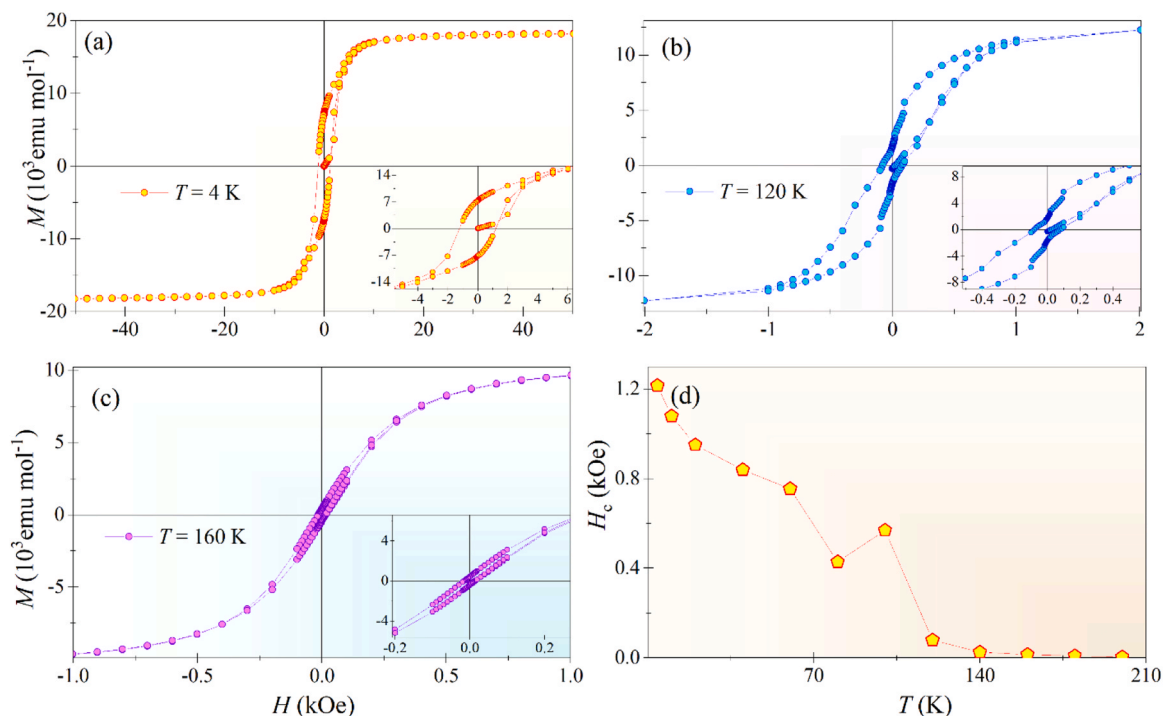


Fig. 7. (a, b, c) Magnetization (M) vs. magnetic field (H) hysteresis loops of Cr_2Fe_4 measured at $T = 4, 120$, and 160 for the ZFC mode. (d) Temperature variation of magnetic coercivity H_c of Cr_2Fe_4 as obtained from the hysteresis loop.

exchange interactions stabilize collinear spin alignment, producing clear hysteresis with finite coercivity (H_c) and remanence. With increasing temperature, thermal fluctuations progressively weaken the exchange coupling, leading to partial spin misalignment. By 160 K , the unsaturated loop suggests spin canting, most likely arising from competing

superexchange interactions. The increasingly linear high-field region reflects a gradual transition toward paramagnetic behaviour as thermal energy destabilizes long-range FM order. Such features are typical of systems where spin-orbit coupling or cation redistribution influence magnetic anisotropy and exchange interactions.

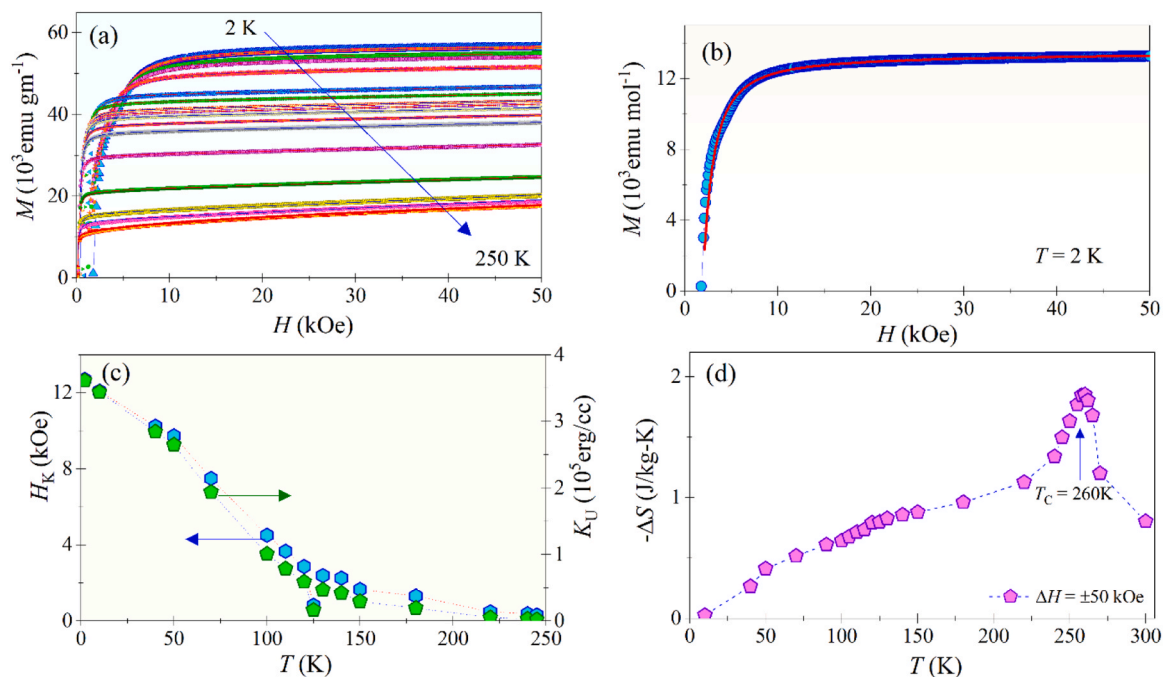


Fig. 8. (a) First quadrant magnetization (M) vs. field (H) isotherms measured at several temperatures ($2 - 250 \text{ K}$). The solid lines represent the best fitted to the Law of Approach to Saturation (LAS) equation. (b) The First quadrant M vs. H isotherm measured particularly at $T = 2 \text{ K}$ with the solid line that represents the best fit to LAS equation. (c) Temperature variation ($2 - 250 \text{ K}$) of cubic anisotropy constant K_U (right hand scale) and the anisotropy field H_K (left hand scale) of Cr_2Fe_4 sample obtained from the LAS fitted parameters. (d) Temperature dependence of the entropy change $-\Delta S$ obtained from the M vs. H isotherms of Cr_2Fe_4 compound using Maxwell equations for a field change $\Delta H = \pm 50 \text{ kOe}$.

Interestingly, Cr₂Fe₄ exhibits an additional feature at low temperature: the virgin (first-quadrant) magnetization curve lies outside the main loop up to $T_A \sim 120$ K. This behaviour, also reported in pristine MCO and the related compound Cr_{0.1}Mn_{0.9}Fe_{0.2}Co_{1.8}O₄, suggests that the magnetic crystalline anisotropy field (H_K) exceeds the coercivity (H_C) in this regime [29,54]. Above $T_A \sim 120$ K, both H_K and H_C become negligible, resulting in conventional hysteresis behaviour, as confirmed by the H_C and H_K variation in Figs. 7(d) and 8(c) respectively.

The isothermal M vs. H curves measured under ZFC conditions between 2 and 250 K (Fig. 8(a)) were fitted using the Law of Approach to Saturation (LAS) [68]: $M = M_S [1 - (a/H) - (b/H^2)] + \chi H$, where a , b and χ are constants, and M_S is the saturation magnetization. Fits were performed with Origin software (solid lines in Fig. 8(a)). The LAS model, initially justified for polycrystalline ferromagnets [68], has been reinforced by subsequent theoretical work [69–72], which attributes the a/H , b/H^2 , and χH terms to magnetocrystalline anisotropy for fields applied along non-easy or non-hard directions. At sufficiently high fields, the b/H^2 term dominates. From LAS fits, the anisotropy field and constant were extracted using $H_K = (105b/2) = 2K_U/M_S$. For example, at 2 K, the fit yields $M_S = 13266(5)$ emu mol⁻¹ (Fig. 8(b)) as shown separately. The temperature dependence of H_K and K_U (Fig. 8(c)) shows a monotonic decrease with increasing temperature.

The magnetocaloric effect (MCE) of Cr₂Fe₄ was evaluated using Maxwell's relation: $\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H$. The temperature variation of $\Delta S_M(H, T) = \int_{H_i}^{H_f} \frac{\partial M}{\partial T} dH$ is shown in Fig. 8(d). A maximum entropy changes of ~ 1.9 J/kg K occurs near the Curie temperature (T_C) for $\Delta H = \pm 50$ kOe. The relative cooling power (RCP), defined as $\int_{T_1}^{T_2} \Delta S_{M,H} dT$ or $\Delta S_M(T) \times \text{FWHM}$ reaches ~ 50 J/kg, where FWHM is the full width at half maximum. This value is comparable to that of other spinel oxides such as CuMn₂O₄ and NiCeFeO₄ [73,74]. Although modest, this performance near room temperature highlights Cr₂Fe₄ as a potential candidate for magnetic refrigeration.

To probe critical behaviour, the spontaneous magnetization (M_S) below T_C and the inverse susceptibility (χ_0^{-1}) above T_C were analysed:

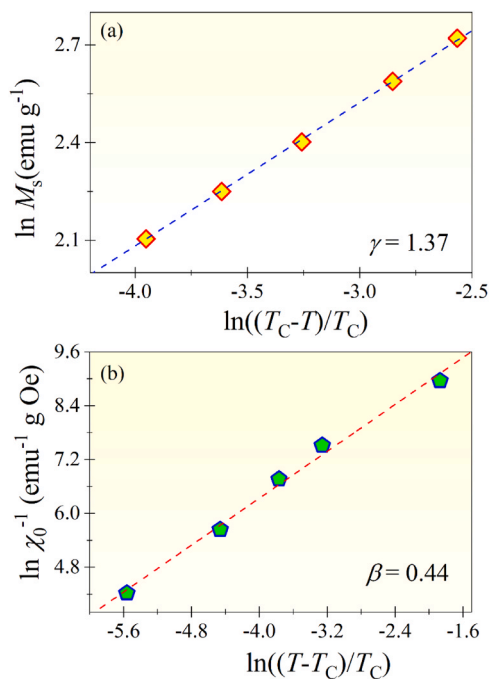


Fig. 9. (a) Plot of $\ln(M_S)$ vs. $\ln[(T_C - T)/T_C]$ and (b) $\ln(\chi_0^{-1})$ vs. $\ln[(T - T_C)/T_C]$ for the Cr₂Fe₄ sample. The dotted lines represent best linear fits with the parameters listed inside.

$$M_S(T < T_C, H \rightarrow 0) = M_0(-\epsilon)^\beta \quad (6)$$

$$\chi_0^{-1}(T > T_C, H \rightarrow 0) = \Gamma(\epsilon^\gamma) \quad (7)$$

Here, $\epsilon = (T - T_C)/T_C$. Using $T_C = 260$ K, the $\ln(M_S)$ vs. $\ln[(T_C - T)/T_C]$ and $\ln(\chi_0^{-1})$ vs. $\ln[(T - T_C)/T_C]$ plots (Fig. 9(a, b)) yield the critical exponents $\beta = 0.44$ and $\gamma = 1.37$. Further, from the Widom scaling law $\delta = 1 + \frac{\gamma}{\beta}$ one finds $\delta \sim 3.11$.

For comparison, the following theoretical predictions are: mean-field ($\beta = 0.5$, $\gamma = 1$, $\delta = 3$), 3D-Ising ($\beta = 0.325$, $\gamma = 1.24$, $\delta = 4.81$), and 3D-Heisenberg ($\beta = 0.365$, $\gamma = 1.336$, $\delta = 4.6$) [75,76]. The obtained β and δ values align more closely with mean-field behaviour, while γ is consistent with the 3D-Heisenberg model. Such mixed characteristics are reasonable, as Cr₂Fe₄ is a ferrimagnet rather than an ideal ferro- or antiferromagnet. More precise testing would require additional data in the narrow critical region $\epsilon = (T - T_C)/T_C < 0.1$.

5. Optical energy bandgap

The optical properties of the investigated systems Cr₂Fe₄ have been probed by means of the diffuse reflectance spectroscopy (DRS) aiming to find the magnitude of bandgap (E_G). To the best of our understanding, such a systematic analysis of the optical bandgap for such Cr/Fe codoped MCO compound Cr₂Fe₄ has not been reported yet. The optical absorbance was measured as a function of photon energy ($h\nu$) for Cr₂Fe₄ compound is known in Fig. 10 (a). To obtain the value of E_G of Cr₂Fe₄ compound, we employed Kubelka-Munk (KM) model of optical absorption. Based on this model, the band structure can be designated by means of KM equation as: $[F(R_\infty) h\nu]^n = \alpha(h\nu - E_G)$ [77]. Here, R_∞ represents the reflectance of the sample, $F(R_\infty)$ the KM function, α signifies the absorption coefficient and n denotes the bandgap index. Here n varies with λ , which follows a value 2 and 1/2 corresponding to direct and indirect bandgap respectively. For any wavelength $F(R_\infty)$ is defined as the ratio between the absorption (K) and the scattering coefficient (S)

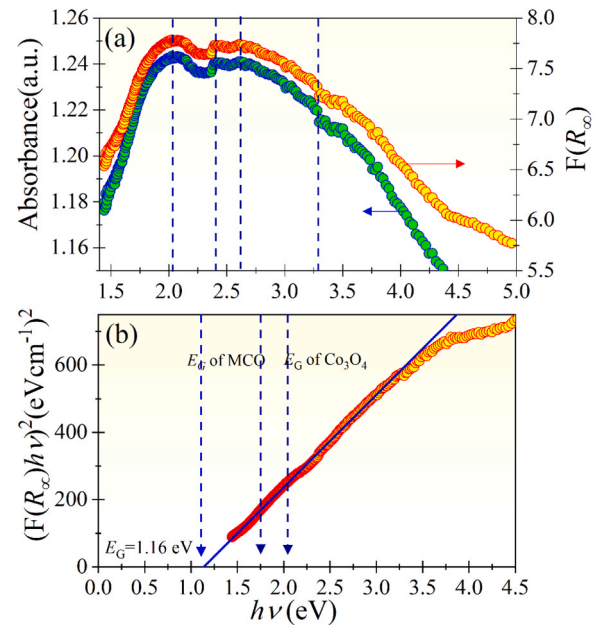


Fig. 10. (a) The absorbance coefficient (left hand scale) and the Kubelka-Munk (KM) function, $F(R_\infty)$ (right hand scale) are represented as a function of photon energy $h\nu$ for Cr₂Fe₄ compound. (b) The plot of the $[F(R_\infty) h\nu]^2$ vs. photon energy $h\nu$ to estimate the optical bandgap (E_G) from the intercept of the linear extrapolation of the Cr₂Fe₄ compound. The different arrows denoted with blue, and black colour represent the E_G values corresponding to Cr₂Fe₄, MCO with a crystallite size (d) ~ 112 nm and Co₃O₄ bulk polycrystalline respectively [77,78].

as $F(R_{\infty}) = K/S = (1 - R_{\infty})^2/2R_{\infty}$. The dependence of $F(R_{\infty})$ on the photon energy $h\nu$ for the investigated compound Cr₂Fe₄ is shown in the right-hand scale of Fig. 10(a). In case of a semiconductor the direct bandgap follows the relation $ah\nu \propto (h\nu - E_g)^2$. For an entirely diffused light, the absorption coefficient $K = 2\alpha$. Taking the scattering coefficient S as constant with λ , the relation to obtain energy band gap becomes $[F(R_{\infty}) h\nu]^n \propto [h\nu - E_g]$. Using this equation, we obtain the direct band gap for most of the semiconducting spinel oxides by plotting the variation of $[F(R_{\infty}) h\nu]^2$ with respect to photon energy $h\nu$ (as shown in Fig. 10 (b)). The extrapolation at the linear region to the energy axis of this curve (as shown in Fig. 10 (b)) results in the magnitude of E_g which is ~ 1.16 eV for Cr₂Fe₄. The similar analysis using $n = 1/2$ (for indirect case) yielded negative E_g value indicating the absence of indirect bandgap variation of electronic structure. Hence, we exclude to show this analysis here rather stick to the analysis pertaining to the direct energy bandgap variation in Cr₂Fe₄. Similar analysis was also applied for bulk Co₃O₄, yielding a direct bandgap $E_g \sim 2.19$ eV [78]. The nanostructures of MCO with $d \sim 112$ nm has slightly larger $E_g \sim 1.73$ eV (blue shifted due to the quantum size effects) [77]. Blue arrows were used to represent these reported E_g values corresponding to its pristine compound MCO as well as its sister compound Co₃O₄ polycrystalline sample for comparison. As the crystallite size d decreases, such blue shift enhances up to 2.4 eV for 5.4 nm MCO. In the present case the coexistence of both trivalent and divalent electronic states of Co and Fe contributes to the formation of conduction band including the trivalent Mn and Cr. A weak transition observed at 3.3 eV in the absorption spectrum is mainly originating from ligand to metal charge transfer processes, similarly to the pristine compound of this series and nanosized Co₃O₄. However, in Co₃O₄ case this transition splits into two parts corresponds to electronic levels of Co³⁺ and Co²⁺ [79]. In the present case the absorption spectra show two sub bands near 2.1 eV (590.5 nm), 2.4 eV (516.6 nm) which are attributed to the charge transfer in between of the d orbital of transition metals: $Mn^{3+}(t_{2g}^3e_g^1) \leftrightarrow Cr^{3+}(t_{2g}^3) \leftrightarrow Fe^{3+}(t_{2g}^3e_g^2) \leftrightarrow Co^{2+}(t_{2g}^5e_g^2)$. In addition to this feature a weak shoulder at 2.6 eV has also been noticed which is associated with the intra-band metal-to-metal type charge transition between the d states due to the crystal-field splitting consistent with the case of pristine MCO [77].

6. Conclusions

In this study, we have investigated the magnetic properties of the Cr and Fe substituted MnCo₂O₄ system at Mn and Co sites realizing the following composition Cr_{0.2}Mn_{0.8}Fe_{0.4}Co_{1.6}O₄. However, a detailed analysis of crystal and magnetic structures using synchrotron XRD (SXRD) and Neutron powered diffraction (NPD) studies reveal the following cationic distribution (Co_{0.975(4)}Fe_{0.025(4)})_A [Cr_{0.20}Mn_{0.80}Fe_{0.375(4)}Co_{0.625(4)}]_BO₄ which is consistent with the magnetization measurements. A distinct descending order in the bond length $\Delta d(A-O) = 0.0046(5)$ from 230 to 150 K has been noticed in both the SXRD and NPD, indicating the magnetoelasticity features in AO₄ tetrahedra. Magnetization data reveals typical ferrimagnetic, FiM character ($T_C = 260$ K) with the following anomalous changes: with decrease in temperature from room temperature, domains order in two steps transitions at $T_{S1} = 114$ K and $T_{S2} = 173$ K due to the onset of magnetoelastic effects. Clear anomalies are noticed across T_C , T_{S1} and T_{S2} in the temperature dependence of lattice parameters $a(T)$. A pronounced frequency dispersion observed in $\chi_{ac}(\omega, T)$, indicates significant dynamic magnetic behavior near and below the T_C . The intra and inter exchange constants $J_{AA}/k_B = 23.2$ K, $J_{BB}/k_B = 9.15$ K and $J_{AB}/k_B = 25.25$ K derived from the Néel's two sublattice model for ferrimagnets are consistent with the typical trend $J_{AB} > J_{AA}$, J_{BB} , as observed for majority of the Mn-based O₄ systems. The critical exponents obtained near to T_C from isothermal magnetization data yields the following values $\beta = 0.44$, $\gamma = 1.37$ and $\delta \sim 3.11$ which resembles to the systems in between of Ising model and 3D-Heisenberg model.

Core-level x-ray photoelectron spectroscopy, combined with optical

absorbance measurements—particularly those probing $d-d$ electronic transitions—provides compelling evidence for the presence of Mn³⁺ (Jahn–Teller active) and Cr³⁺ ions in the studied system. In contrast, Fe and Co ions exhibit mixed-valence behavior, with both Fe²⁺/Co²⁺ and Fe³⁺/Co³⁺ oxidation states coexisting. This mixed-valence character contributes to the formation of an electronic band gap (E_g) of approximately 1.16 eV, situated between the valence and conduction bands.

CRediT authorship contribution statement

Thota Subhash: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **R. Mathieu:** Writing – review & editing, Data curation, Conceptualization. **Kaushik S. D.:** Writing – review & editing, Formal analysis, Data curation, Conceptualization. **R. Athira:** Writing – review & editing, Data curation, Conceptualization. **T. Sarkar:** Writing – review & editing, Data curation, Conceptualization. **Többsen D. M.:** Writing – review & editing, Formal analysis, Data curation, Conceptualization. **M. Reehuis:** Writing – review & editing, Formal analysis, Data curation, Conceptualization. **P. Pramanik:** Writing – review & editing, Investigation, Data curation, Conceptualization. **Singha A. D.:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Resources, Methodology, Formal analysis, Data curation, Conceptualization.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Dr. Subhash Thota reports financial support, administrative support, equipment, drugs, or supplies, and writing assistance were provided by Indian Institute of Technology Guwahati. Dr. Subhash Thota reports a relationship with Indian Institute of Technology Guwahati that includes: employment. 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. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

S.T. and A.D.S. express since thanks to Prof. M. S. Seehra (Eberly Distinguished Professor Emeritus), Department of Physics and Astronomy, West Virginia University (WVU) for his helpful discussions. S.T. and A.D.S. gratefully acknowledge the financial support from the DST-SERB Core Research Grant (File No. CRG/2022/006155). They also acknowledge partial support from the FIST program of the Department of Science and Technology, India (Grant Nos. SR/FST/PSII-020/2009 and SR/FST/PSII-037/2016). S.T. and A.D.S. thank the Central Instrument Facility (CIF), Indian Institute of Technology Guwahati, for providing access to instrumentation facilities, and the HZB Berlin KMC-2 beamline at the BESSY II synchrotron source for structural characterization. T.S. acknowledges financial support from the Swedish Research Council (VR Grant No. 2021–03675). S.T. further acknowledges the *Invité Professor* fellowship from Université de Caen. A.D.S. also thanks the North East Centre for Biological Sciences and Healthcare Engineering (NECBH), IIT Guwahati, and the Department of Biotechnology (DBT), Govt. of India (Project No. BT/NER/143/SP44675/2023), for partial support.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2026.187534.

Data availability

All data have been included in the manuscript as well as in the [Supplementary Information \(SI\)](#). The SI section contains plots related to the synchrotron x-ray diffraction at different temperatures along with microstructure analysis using FESEM image. Also, information related to the ac-magnetic susceptibility data and the corresponding optimized analysis of relaxation time as a function of temperature related to both the empirical scaling-laws such as Power-law of critical scaling down and Vogel-Fulcher law are shown in SI section.

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