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Nature of Magnetic Ordering in Cobalt-Based Spinels

Subhash Thota and Sobhit Singh

Abstract

In this chapter, the nature of magnetic ordering in cobalt-based spinels Co$_3$O$_4$, Co$_2$SnO$_4$, Co$_2$TiO$_4$, and Co$_2$MnO$_4$ is reviewed, and some new results that have not been reported before are presented. A systematic comparative analysis of various results available in the literature is presented with a focus on how occupation of the different cations on the A- and B-sites and their electronic states affect the magnetic properties. This chapter specifically focuses on the issues related to (i) surface and finite-size effects in pure Co$_3$O$_4$, (ii) magnetic-compensation effect, (iii) co-existence of ferrimagnetism and spin-glass-like ordering, (iv) giant coercivity ($H_C$) and exchange bias ($H_{EB}$) below the glassy state, and (v) sign-reversal behavior of $H_{EB}$ across the ferri/antiferromagnetic Néel temperature ($T_N$) in Co$_2$TiO$_4$ and Co$_2$SnO$_4$. Finally, some results on the low-temperature anomalous magnetic behavior of Co$_2$MnO$_4$ spinels are presented.

Keywords: ferrimagnetic materials, Néel temperature, spin-glass, exchange bias

1. Introduction

The atomic arrangement of the spinel compounds is interpreted as a pseudo-close-packed arrangement of the oxygen anions with divalent cations occupying tetrahedral A-sites and trivalent cations residing at the octahedral B-sites of the cubic unit cell of space group Fd-3m(227). A spinel with the configuration (A$^{2+}$) [B$^{3+}$] O$_4$ is termed as “normal spinel” whereas the other possible configuration (B$^{3+}$) [A$^{2+}$B$^{3+}$] O$_4$ is called “inverse spinel.” The continuum of possible atomic distribution between these two extremes is quantified by a parameter denoted as $x$ (inversion parameter), which describes the fraction of “B” cations on tetrahedral sites. Thus, $x = 0$ for a normal spinel, 2/3 for a spinel with entirely arbitrary configuration, and 1 for a fully inverse spinel. Among many varieties of spinel compounds,
ferrites and cobaltites are widely used in the high-frequency electronic circuit components such as transformers, noise filters, and magnetic recording heads [1, 2]. The key property of these spinels is that at high frequencies (>1 MHz), their dielectric permittivity ($\varepsilon$) and magnetic permeability ($\mu$) are much higher than those of metals with low loss-factor ($\tan\delta$). These properties make them very advantageous for the development of magnetic components used in the power electronics industry. Also, the nanostructures of these spinels continue to receive large attention because of their potential applications in solid-oxide fuel cells, Li-ion batteries, thermistors, magnetic recording, microwave, and RF devices [1, 2].

In this review, we mainly focus on the nature of magnetic ordering of several insulating cobalt spinels of type Co$_2$M$\text{O}_4$ (where “M” is the tetravalent or trivalent metal cation such as Sn, Ti, Mn, Si, etc.) which are not yet well studied in literature. This review will primarily illustrate how the magnetic ordering changes when we substitute the above-listed metal cations at the tetrahedral B-sites. It is well known that the dilution of magnetic elements significantly disrupts the long-range magnetic ordering and leads to more exotic properties like magnetic frustration, polarity reversal exchange bias, and reentrant spin-glass state near the magnetic-phase transition [3, 4]. The dilution essentially alters the super-exchange interactions of $J_{\text{AB}}$, $J_{\text{BB}}$, and $J_{\text{AA}}$ between the magnetic ions, which is the main source of anomalous magnetic behavior.

In this review, we first start with the simplest case of antiferromagnetic (AFM) normal-spinel Co$_3$O$_4$ with configuration (Co$^{2+}$)[Co$^{3+}$]O$_4$ and discuss the role of surface and finite-size effects on antiferromagnetic (AFM) ordering. In the second section, we focus on the coexistence of ferrimagnetism and low-temperature spin-glass behavior of cobalt orthostannate (Co$_2$SnO$_4$) and cobalt orthotitanate (Co$_2$TiO$_4$). A detailed comparative analysis of some recent experimental results dealing with the temperature and frequency dependence of ac-magnetic susceptibility is presented. In the subsequent section, some unusual magnetic properties of Co$_2$MnO$_4$ are discussed.

2. Magnetic properties of bulk versus nanocrystalline Co$_3$O$_4$

Cobalt forms two binary compounds with oxygen: CoO and Co$_3$O$_4$. While CoO has face-centered cubic (NaCl-type) structure, Co$_3$O$_4$ shows a normal-spinel structure with a cubic close packed arrangement of oxygen ions and Co$^{2+}$ and Co$^{3+}$ ions occupying the tetrahedral “8a” and the octahedral “16d” sites, respectively [5]. The magnetic properties of Co$_3$O$_4$ were first investigated over 58 years ago; however, its magnetic behavior under reduced dimensions still attracted immense scientific interest mainly because of its distinctly different magnetic ordering under nanoscale as compared to its bulk counterpart [6]. Co$_3$O$_4$ can be synthesized in various nanostructural forms such as nanorods, nanosheets, and ordered nanoflowers with ultrafine porosity [7–10]. Such engineered nanostructures play vital roles as catalysts, gas sensors, magneto-electronics, electrochromic devices, and high-temperature solar selective absorbers [11–18]. At first glance, the normal-spinel structure of Co$_3$O$_4$ may look similar to that of Fe$_3$O$_4$ (inverse spinel) but Co$_3$O$_4$ exhibits strikingly different magnetic ordering as compared to Fe$_3$O$_4$. In particular, Co$_3$O$_4$ does not exhibit ferrimagnetic ordering of the type observed in Fe$_3$O$_4$ because Co$^{3+}$ ions on the octahedral B-sites are in the low spin $S = 0$ state [5].
Instead, it exhibits antiferromagnetic ordering with each Co$^{2+}$ ion at the A-site having four neighboring Co$^{2+}$ ions of opposite spins (with an effective magnetic moment of $\mu_{\text{eff}} \sim 4.14 \mu_B$) [5]. Earlier studies by Roth reported that below the Néel temperature $T_N \sim 40$ K, Co$_3$O$_4$ becomes antiferromagnetic in which the uncorrelated spins of the 8Co$^{2+}$ (in 8(a), F.C. +000, 111 444) cations in the paramagnetic state (space group O’h—Fd-3m) are split in the antiferromagnetic state (space group T$d$—F43m) into the two sublattices with oppositely directed spins of 4Co$^{2+}$ $\uparrow$ (4(a), +000) and 4Co$^{2+}$ $\downarrow$ (4(c) 111 444) [5–7]. For $T < T_N$, the neutron diffraction studies did not show any evidence of a structural phase transition.

As shown in Figure 1, the recent magnetic studies by Dutta et al. [6] have reported a significant difference in the antiferromagnetic ordering temperature $T_N \sim 30$ K of Co$_3$O$_4$ as compared to the earlier data (40 K); this new result however is in excellent agreement with $T_N = 29.92 \pm 0.03$ K obtained by the heat capacity $C_p$ versus $T$ measurements reported by Khriplovich et al. [19]. It is well known that the peak in the magnetic susceptibility data of antiferromagnets usually occurs at a temperature few percent higher than $T_N$ because the magnetic specific heat of a simple antiferromagnet (in particular, the singular behavior in the region of the transition) should be closely similar to the behavior of the function $d(\chi_p T)/dT$ [14]. Therefore, $T_N$ is better

![Figure 1](http://dx.doi.org/10.5772/65913)

**Figure 1.** (a) Temperature dependence of the dc-magnetic susceptibility $\chi(T)$ for bulk Co$_3$O$_4$ under the zero-field-cooled (ZFC) and field-cooled (FC) conditions. Here, $T_p$ denotes the peak position in $\chi$ versus $T$ plots. (b) Plots of ($\chi_p T$) versus $T$ (LHS scale) and $d(\chi_p T)/dT$ versus $T$ plots (RHS scale) for the bulk Co$_3$O$_4$. Here, the paramagnetic susceptibility $\chi_p = \chi - \chi_0$ with $\chi_0 = 3.06 \times 10^{-6}$ emu/g Oe being the temperature-independent contribution [6, 7].
defined by the peak in $\partial(\chi_p)/\partial T$ versus $T$ plot [20]. Figure 1 shows the temperature dependence of paramagnetic susceptibility $\chi_p (T)$ (LHS scale) and $d(\chi_p T)/dT$ versus $T$ (RHS scale). For bulk Co$_3$O$_4$, the peak temperature value (30 K) in the $d(\chi_p T)/dT$ versus $T$ plots is lower than $T_N \approx 40$ K often quoted for Co$_3$O$_4$ [5–7, 9–10]. Thus, $T_N = 30$ K determined from two independent techniques (i.e., $\chi_p$ and $C_p$ measurements) is consistent with each other and is the accurate characteristic value for bulk Co$_3$O$_4$. On the other hand, the nanoparticles of Co$_3$O$_4$ exhibit lower $T_N$ values and reduced magnetic moment than the bulk value (30 K, 4.14 $\mu_B$) which is a consequence of finite-size and surface effects [6]. Salabas et al. first reported Co$_3$O$_4$ nanowires of diameter 8 nm and lengths of up to 100 nm by the nanocasting route and observed $T_B \approx 30$ K and exchange bias ($H_e$) for $T < T_B$ [10].

Figure 2. Variation of the Néel temperature $T_N$ of Co$_3$O$_4$ as a function of particle size ($d$). The data pertaining to solid-square symbols are taken from Refs. [6–8] in which $T_N$ is considered as a peak point in “$d(\chi_p T)/dT$ versus $T$” data. However, the data related to solid green circles are taken from Refs. [8, 9] in which $T_N$ is considered as just the peak point in the “$\chi$ versus $T$” plot, not from the derivative plots. The scattered symbols are the raw data corresponding to $T_N$ and the solid lines are the best fit to Eq. (1).

A plot of $T_N$ values versus particle size $d$ reported by several authors for various crystallite sizes of Co$_3$O$_4$ is shown in Figure 2. The lowest $T_N$ value reported till now is about 15 ± 2 K for 4.34 nm size Co$_3$O$_4$ particles [8]. These nanoparticles were synthesized using biological containers of Listeria innocua Dps proteins and LDps as constraining vessels. Lin and Chen studied the magnetic properties of various sizes (diameter $d = 16, 35,$ and 75 nm) of Co$_3$O$_4$ nanoparticles prepared by chemical methods using CoSO$_4$ and CoCl$_2$ as precursors [9]. These authors reported that the variation of $T_N$ follows the finite-size scaling relation:
for various sizes of Co₃O₄ nanoparticles. Accordingly, they obtained the shift exponent \( \lambda = 1.1 \pm 0.2 \) and the correlation length \( \xi_\infty = 2.8 \pm 0.3 \) nm from the fitting analysis of \( T_N \) versus \( d \) (Figure 2). However, these authors considered \( T_N \) values as the direct peak temperature values from \( \chi \) versus \( T \) instead of the peak point in \( d(\chi_p T)/dT \). Also, for the bulk grain sizes \( T_N(\infty) = 40 \) K was considered instead of 30 K obtained from \( d(\chi_p T)/dT \) analysis as discussed above. Therefore, we repeated the analysis but considering \( T_N \) values obtained from \( d(\chi_p T)/dT \) versus \( T \) and the \( T_N(\infty) = 30 \) K for various sizes of the Co₃O₄ nanoparticles obtained by sol-gel process (these values were obtained from our earlier works [6, 7]). Accordingly, we obtained \( \lambda = 1.201 \pm 0.2 \) and the correlation length \( \xi_\infty = 2.423 \pm 0.46 \) nm, which are slightly different from the earlier reported values \( \lambda = 1.1 \pm 0.2 \) and the correlation length \( \xi_\infty = 2.8 \pm 0.3 \) nm [9]. Nonetheless, in both the cases \( T_N \) follows the finite-size scaling relation Eq. (1).

For \( T > T_N \), the data of \( \chi \) versus \( T \) (Figure 3) are fitted to the modified Curie-Weiss law \( \chi_p = \chi_0 + [C/(T + \theta)] \) with \( C = N\mu^2/3k_B \mu^2 = g^2 J(J + 1)\mu_B^2 \), \( \theta \) is the Curie-Weiss temperature and \( \chi_0 \) contains two contributions: the temperature-independent orbital contribution mentioned earlier and

\[
T_N(D) = T_N(\infty) \left[ 1 - \left( \frac{\xi_\infty}{d} \right)^\lambda \right]
\]

(1)

Figure 3. \( 1/\chi_p \) versus \( T \) plots for the bulk and nanocrystalline (\( \sim 17 \) nm) Co₃O₄ with \( \chi_0 = 3.06 \times 10^{-6} \) emu/g Oe (LHS scale). The solid lines represent linear fit to the Curie-Weiss law: \( \chi_\infty = C/(T + \theta) \). On the RHS scale same figures are plotted except for \( \chi_0 = 9 \times 10^{-6} \) and \( 7.5 \times 10^{-6} \) emu/g Oe for the bulk and Co₃O₄ nanoparticles of size \( \sim 17 \) nm, respectively [6, 7].
the diamagnetic component \( \chi_d = -3.3 \times 10^{-7} \) emu/g Oe [6]. Usually \( \chi_0 \) is estimated from the plot of \( \chi \) versus \( 1/T \) in the limit of \( 1/T \rightarrow 0 \) using the high-temperature data. The value of \( \chi_0 \) was estimated as \( 3.06 \times 10^{-6} \) emu/g Oe for bulk Co\(_3\)O\(_4\) using the inverse paramagnetic susceptibility \( (1/\chi_P) \) versus temperature \( (T) \) data (shown in the left-hand-side scale of Figure 3) [5, 6]. A similar procedure for experimental data, shown in the right-hand side scale of Figure 3, yields \( \chi_0 = 9 \times 10^{-6} \) and \( 7.5 \times 10^{-6} \) emu/g Oe for the bulk and nanoparticles (size \( \sim 17 \) nm) of Co\(_3\)O\(_4\), respectively.

It is well known that the origin of the antiferromagnetic ordering in transition metal oxides can be explained by the super-exchange interaction between the magnetic elements via oxygen ion. In the present case, there are two possible paths for super-exchange interaction between magnetic ions in Co\(_3\)O\(_4\) i.e., Co\(^{2+}\) ions: (tetrahedral site) A – O (oxygen) – A (tetrahedral site) and A – O – B – O – A with the number of nearest-neighbors \( z_1 = 4 \) and next-nearest-neighbors \( z_2 = 12 \), respectively. If the corresponding exchange constants are represented by \( J_{1ex} \) and \( J_{2ex} \), the expressions for \( T_N \) and \( \theta \), using the molecular-field theory, can be written as [5, 6]

\[
T_N = \frac{J(J+1)}{3k_B} \left( J_{1ex} z_1 - J_{2ex} z_2 \right)
\]

(2)

\[
\theta = \frac{J(J+1)}{3k_B} \left( J_{1ex} z_1 + J_{2ex} z_2 \right)
\]

(3)

In order to determine \( J_{1ex} \) and \( J_{2ex} \), the magnitude of effective \( J(J+1) \) for Co\(^{2+}\) is required. Since the Curie constant \( C \) is equivalent to \( N \mu^2/3k_B \) with \( \mu = g [J(J+1)]^{1/2} \mu_B \) where \( g \) is the Landé \( g \)-factor and \( J \) is the total angular momentum. Using the magnitude of \( g = 2 \) and \( C \) from Figure 3, one can estimate the effective magnetic moment \( \mu_{eff} = 4.27 \mu_B \) for bulk Co\(_3\)O\(_4\) and \( \mu = 4.09 \mu_B \) for Co\(_3\)O\(_4\) nanoparticles of size \( \sim 17 \) nm. The spin contribution to the above magnitudes of \( \mu \) is 3.87 \( \mu_B \) for Co\(^{2+}\) with spin \( S = 3/2 \). Obviously, there is some additional contribution resulting from the partially restored orbital angular moment for the \( ^4F_{9/2} \) ground state of Co\(^{2+}\) [5, 6]. Using Eqs. (2) and (3) and the values of “\( \theta \),” “\( T_N \),” and “\( \mu \)” for the two cases yields \( J_{1ex} = 11.7 \) and \( J_{2ex} = 2.3 \) K for bulk, and \( J_{1ex} = 11.5 \) and \( J_{2ex} = 2.3 \) K for the Co\(_3\)O\(_4\) nanoparticles (\( d \sim 17 \) nm). Thus, both the exchange constants \( J_{1ex} \) and \( J_{2ex} \) correspond to antiferromagnetic coupling. From the magnitudes of \( \mu \) in Figure 3, the value of \( \mu \) is obtained as 3.28 and 3.43 \( \mu_B \) for bulk and Co\(_3\)O\(_4\) nanoparticles (\( d \sim 17 \) nm), respectively. These magnitudes of \( \mu \) are lower than the spin contribution (3.87 \( \mu_B \)) of Co\(^{2+}\) ion itself. Consequently, the magnitudes of “\( \theta \)” in Figure 3 seem to be questionable. This may be due to the fact that the use of molecular-field theory in determining the exchange constants has its own limitations since higher order spin correlations are neglected in this model [6].

For a typical bulk antiferromagnet, below \( T_N \), the magnetization is expected to vary linearly with applied external magnetic field \( H \) below the spin-flop field. Therefore, the corresponding coercive field \( H_c \) and exchange-bias field \( H_e \) must become zero. This was indeed observed in bulk Co\(_3\)O\(_4\) (Figure 4a) [5, 6]. Conversely, for the Co\(_3\)O\(_4\) nanoparticles (\( d \sim 17 \) nm), the data at
5 K show a symmetric hysteresis loop with $H_c = 200$ Oe for the zero-field-cooled sample and asymmetric (shifted) hysteresis loop with $H_c = 250$ Oe and $H_e = −350$ Oe for the sample cooled in magnetic field $H = 20$ kOe from 300 to 5 K as shown in Figure 4b. Thus, cooling the sample in a magnetic field produces an exchange bias and leads to the enhancement of $H_c$ as well. The temperature dependence of $H_c$ and $H_e$ for the nanoparticles of Co$_3$O$_4$ cooled under $H = 20$ kOe from 300 K to the measuring temperature is shown in Figure 5. Both $H_c$ and $H_e$ approach to zero above $T_N$. The inset of Figure 5 depicts the training effect, i.e., change in the magnitude of $H_e$ for the sample cycled through several successive hysteresis loops (designated by “n” at 5 K) [6, 10]. A similar effect has been recently reported by Salabas et al. [10] in the Co$_3$O$_4$ nanowires of 8 nm diameter although the magnitudes of $H_c$ and $H_e$ in their case are somewhat smaller. The existence of the exchange bias suggests the presence of a ferromagnetic (shell)/antiferromagnetic (core) interface with FM-like surface spins covering the core of antiferromagnetically ordered spins in the nanoparticles of Co$_3$O$_4$. Salabas et al. reported that $H_e$ falls by ~25% measured between the first and the second loops. The observation of the training effect and open loops of up to 55 kOe suggests that the surface spins are in an unstable spin-glass-like state [10]. Such a spin-glass ordering results from the weaker exchange coupling experienced by the surface spins due to reduced coordination at the surface. These effects however disappear above $T_N$ when the spins in the core become disordered. The observation
of somewhat lower magnetic moment per Co$^{2+}$ ion, smaller values of exchange constants $J_{1ex}$ and $J_{2ex}$ and lower $T_N$ was noticed for the nanoparticles of Co$_3$O$_4$ in relation to the bulk Co$_3$O$_4$. This could be due to the weak exchange coupling and reduced coordination of the surface spins.

Figure 5. The temperature dependence of $H_c$ and $H_e$ for the nanoparticles of Co$_3$O$_4$ ($d \sim 17$nm) measured from $T = 5$ to 40 K under field-cooled (FC) mode at 20 kOe and at 5 K under zero-field-cooled (ZFC) condition [6]. One can clearly notice $H_c \to 0$, $H_e \to 0$ as $T$ approaches $T_N$. The inset shows progressive decrease of the magnitude of $H_e$ after successive scan (number of cycles"n") at 5 K [6].

3. Co-existence of ferrimagnetism and spin-glass states in some inverted spinels

In 1975, Sherrington and Kirkpatrick (SK) first predicted the reentrant behavior of spinels using mean-field approach for certain relative values of the temperature and exchange interaction [21, 22]. Later, Gabay and Toulouse extended the SK Ising model calculation to the vector spin glasses and showed that it is possible to have multiple phase transitions such as ferro/ferri/antiferromagnetic state $T_F$ or $T_{AN}$ $T_{MG}$ paramagnetic state $T_{MG}$ Mixed phase-1 $T_{MG}$ Mixed phase-2 [22, 23]. The present section deals with such kind of systems in which the longitudinal ferrimagnetic ordering coexists with the transverse spin-glass state below the Néel temperature $T_N$ [23–28]. In this connection, we mainly focus on the magnetic ordering in two inverse-spinel systems, namely (i) cobalt orthostannate (Co$_2$SnO$_4$) and (ii) cobalt orthotitanate (Co$_2$TiO$_4$) which exhibits the reentrant spin-glass behavior [24–40]. At first glimpse, both systems Co$_2$SnO$_4$ and Co$_2$TiO$_4$ are expected to show similar magnetic properties because of the fact that
nonmagnetic ions Sn and Ti play identical role on the global magnetic ordering of the system. But in reality, they exhibit markedly different magnetic structures below their ferrimagnetic Néel temperatures [24–40], which is discussed in detail below.

Usually, the ferrimagnetic ordering in Co$_2$SnO$_4$ and Co$_2$TiO$_4$ arises from the unequal magnetic moments of Co$^{2+}$ ions at the tetrahedral A-sites and octahedral B-sites [24–40]. The corresponding magnetic moment at the tetrahedral A-sites $\mu(A)$ is equal to 3.87 $\mu_B$, and the magnetic moment at octahedral B-sites $\mu(B)$ is equal to 5.19 and 4.91 $\mu_B$ for Co$_2$TiO$_4$ and Co$_2$SnO$_4$, respectively [27–33]. In 1976, Harmon et al. first reported the low-temperature magnetic properties of polycrystalline Co$_2$SnO$_4$ system and showed the evidence for ferrimagnetic ordering with $T_N \sim 44 \pm 2$ K [24]. They also suggested that Co$_2$SnO$_4$ should contain two equally populated sublattices that align collinearly and couple antiferromagnetically [24]. On the basis of the Mössbauer spectroscopy results, these authors calculated the internal dipolar fields at the Sn sites from the two Co$^{2+}$ sublattices to be $> 80$ kOe [24]. They also reported very high values of coercive field $H_C > 50$ kOe below $T_N$ [24]. The reported magnetization value at 16 K per Co$^{2+}$ ion was about $2.2 \times 10^{-1} \mu_B$ with zero magnetization value at 12 K. The Curie-Weiss constant ($C$) = 4.3 ± 0.2 emu/mol, and the effective magnetic moment of the Co$^{2+}$ ions = 5.0 ± 0.2 $\mu_B$ was close to the standard value of 4.13 emu/mol and 4.8 $\mu_B$, respectively. A year later, Sagredo et al. reported that the zero-field-cooled and field-cooled magnetization curves of single crystal Co$_2$SnO$_4$ exhibit strong irreversibility below $T_N$ [39].

Sagredo et al. reported that thermoremanent magnetization, magnetic training effects, and spin-glass phases present in this system are driven by the disordered-spin configurations [39]. Accordingly, they speculated that the random distribution of Sn$^{4+}$ ions on the B-sites might break the octahedral symmetry of the crystal field and result in the frustrated magnetic behavior [39]. In 1987, Srivastava et al. reported multiple peaks in the temperature dependence of ac-magnetic susceptibility $\chi_{ac}(T)$ for both Co$_2$SnO$_4$ and Co$_2$TiO$_4$ below their $T_N$, providing the evidence of Gabay and Tolouse mixed-phase transitions [25, 28]. Nevertheless, some recent studies proved the existence of transverse spin-glass state $T_{SG}$ ($\sim 39$ K) just below the $T_N$ ($\sim 41$ K) in Co$_2$SnO$_4$ [27, 38, 40]. Similar type of results in Co$_2$TiO$_4$ was reported by Hubsch et al. and Srivastava et al. but with different $T_{SG}$ ($\sim 46$ K) and $T_N$ ($\sim 55$ K) [25, 28, 31, 34].

In order to get a precise understanding of the magnetic properties of these systems, we have plotted the temperature dependence of dc-magnetic susceptibility $\chi_{dc}(T)$ for both Co$_2$SnO$_4$ and Co$_2$TiO$_4$, measured under ZFC and FC (H@100 Oe) conditions in Figure 6. These $\chi_{dc}(T)$ plots show typical characteristics of ferrimagnetic ordering with peaks across the Néel temperatures $T_N = 47$ K (for Co$_2$TiO$_4$) and 39 K (for Co$_2$SnO$_4$). However, for $T \lesssim 31.7$ K an opposite trend in the $\chi_{dc}(T)$ values was noticed for Co$_2$TiO$_4$ with $\chi_{dc} \sim 0$ at magnetic-compensation temperature $T_{CMP} = 31.7$ K at which the two-bulk sublattices magnetizations completely balances with each other [31–33]. Such compensation behavior in Co$_2$SnO$_4$ system is expected to appear at very low temperatures ($T < 10$ K) as $\chi_{dc}(T)$ approaches to zero. Consequently, $\chi_{dc,ZFC}$ exhibits negative magnetization until $T_{SG}$. It is expected that the different magnetic moments on the tetrahedral (A) and the octahedral (B) sites, and their different temperature dependence (i.e., $\mu_A(T)$, $\mu_B(T)$) play a major role on the global magnetic ordering of both systems.
Figure 6. The temperature dependence of dc-magnetic susceptibility $\chi_{dc}(T)$ measured under ZFC and FC (H=100 Oe) conditions for both Co$_2$TiO$_4$ (LHS) and Co$_2$SnO$_4$ (RHS). The dotted line shows the $T_{CMP}$.

Recent X-ray photoelectron spectroscopic studies reveal that the crystal structure of Co$_2$TiO$_4$ consists of some fraction of trivalent cobalt and titanium ions at the octahedral sites, i.e., [Co$^{2+}$][Co$^{3+}$]Ti$^{3+}$O$_4$ instead of [Co$^{2+}$][Co$^{2+}$]Ti$^{4+}$O$_4$ [34]. On the contrary, the Co$_2$SnO$_4$ shows the perfect tetravalent nature of stannous ions without any trivalent signatures of Co$^{3+}$ [Co$^{2+}$][Co$^{2+}$]Sn$^{4+}$O$_4$ [27]. Such distinctly different electronic structure of the ions on the B-sites of cobalt orthotitanate plays a significant role on the anomalous magnetic ordering below $T_N$, for example, exhibiting the magnetic-compensation behavior, sign reversible zero-field exchange-bias, and negative slopes in the Arrott plots ($H/M$ versus $M^2$) [27, 34].

Table 1 summarizes various fitting parameters obtained from the Néel expression for both Co$_2$SnO$_4$ and Co$_2$TiO$_4$. The fit for Co$_2$TiO$_4$ yields the following parameters: $\chi_0 = 41.92 \times 10^{-3}$ emu/mol-Oe, $\sigma_0 = 31.55$ mol-Oe-K/emu, $C = 5.245$ emu K/mol Oe, $T_a = 49.85$ K. The ratio $C/\chi_0 = T_a$ represents the strength of the antiferromagnetic exchange coupling between the spins on the A- and B-sites and is often termed as the asymptotic Curie temperature $T_a$. For both the systems, the effective magnetic moment $\mu_{eff}$ is determined from the formula $C/\chi_0 = N\mu_{eff}^2/3k_B$. The experimentally observed magnetic moments at the B-sites $\mu(B) = 5.19 \mu_B$ obtained from the temperature dependence of magnetization values are in line with the above-discussed spectroscopic properties of Co$_2$TiO$_4$, i.e., the total moment $\mu(B)$ is perfectly matching with the contribution from the magnetic moments due to Co$^{3+}$ (4.89 $\mu_B$) and Ti$^{3+}$ (1.73 $\mu_B$), $\mu(B) = \left(\frac{\mu_{Co^{3+}}}{2}\right)^2 + \left(\frac{\mu_{Ti^{3+}}}{2}\right)^2$ [34]. Also, the analysis of the dc and ac susceptibilities combined with the weak anomalies observed in the $C_p$ versus $T$ data has shown the existence of a quasi-long-range ferrimagnetic state below $T_N = 47.8$ K and a compensation temperature of $T_{CMP} = 32$ K [34].
The real and imaginary components of the temperature dependence of ac-susceptibility data $\chi_{ac}(T) (=\chi'(T) + i \chi''(T))$ recorded at different frequencies for both the polycrystalline samples $\text{Co}_2\text{SnO}_4$ and $\text{Co}_2\text{TiO}_4$ show the dispersion in their peak positions ($T_P(f)$) similar to the compounds exhibiting spin-glass-like ordering [27, 33]. Figure 8 shows the $\chi'(T)$ and $\chi''(T)$ data of $\text{Co}_2\text{SnO}_4$ and $\text{Co}_2\text{TiO}_4$ recorded at different measuring frequencies ranging from 0.17 to 1202 Hz with peak-to-peak field amplitude $H_{ac} = 4$ Oe under zero dc-bias field. It is clear from these figures that the peaks seen in both cases show pronounced frequency dependence, which suggests the dynamical features analogous to that of observed in spin-glass systems. A detailed analysis of such frequency dependence of $\chi'(T)$ and $\chi''(T)$ using two scaling laws described below provides the evidence for spin-glass-like characteristics below $T_N$. For example, applying the Vogel-Fulcher law (below equation) for interacting particles

$$\tau = \tau_0 \exp\left(\frac{E_a}{k_B(T - T_0)}\right)$$

and the best fits of the experimental data (the logarithmic variation of relaxation time”$\tau$" as a function of $1/(T_F - T_0)$ as shown in Figure 8a) yields the following parameters: interparticle interaction strength $T_0 = 39.3$ K and relaxation time constant $\tau_0 = 7.3 \times 10^8$ s for $\text{Co}_2\text{SnO}_4$. Here, we define the freezing temperature for each frequency is $T_F$, angular frequency $\omega$ as $2\pi f (\omega = 1/\tau)$, $k_B$ is the Boltzmann constant, and $E_a$ is an activation energy parameter. Such large value of $\tau_0$ indicates the presence of interacting magnetic spin clusters of significant sizes in the polycrystalline $\text{Co}_2\text{SnO}_4$ system. The origin of such spin clusters may arise from a short-range magnetic order occurring due to the competition between ferrimagnetism and magnetic frustration. Another characteristic feature that the spin-glass systems follows is the power law (Eq. (5)) of critical slowing down in a spin-glass phase transition at $T_{sc}$ (note that the $T_P(f)$ data represent a relatively small temperature interval):

$$\tau \propto \left(\frac{T}{T_0} - 1\right)^{-\nu}$$

### Table 1. The list of various parameters obtained from the Néel fit of $\chi^{-1}$ versus $T$ curve recorded under zero-field-cooled condition.

<table>
<thead>
<tr>
<th>System</th>
<th>$C$ (emu K/mol/Oe)</th>
<th>$\chi_o$ (emu/mol/Oe)</th>
<th>$\sigma_o$ (Oe mol K emu$^{-1}$)</th>
<th>$\theta$ (K)</th>
<th>$\mu_{eff}$ (B)</th>
<th>$\mu$ (A) (B)</th>
<th>$\mu$ (B) (B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Co}_2\text{TiO}_4$</td>
<td>5.245</td>
<td>0.0419</td>
<td>31.55</td>
<td>49.85</td>
<td>6.5</td>
<td>3.87</td>
<td>5.19</td>
</tr>
<tr>
<td>$N_{AA}$</td>
<td>$N_{AB}$</td>
<td>$N_{BB}$</td>
<td>$J_{AA}$</td>
<td>$J_{AB}$</td>
<td>$J_{BB}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17.319</td>
<td>35.700</td>
<td>12.720</td>
<td>3.25</td>
<td>4.47</td>
<td>4.74</td>
<td>3.18</td>
<td></td>
</tr>
<tr>
<td>$\text{Co}_2\text{SnO}_4$</td>
<td>4.889</td>
<td>0.0456</td>
<td>102.370</td>
<td>39.5</td>
<td>6.25</td>
<td>3.87</td>
<td>4.91</td>
</tr>
<tr>
<td>$N_{AA}$</td>
<td>$N_{AB}$</td>
<td>$N_{BB}$</td>
<td>$J_{AA}$</td>
<td>$J_{AB}$</td>
<td>$J_{BB}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21.564</td>
<td>33.201</td>
<td>10.68</td>
<td>4.05</td>
<td>5.26</td>
<td>4.28</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 7(a). The temperature dependence of the ac-magnetic susceptibilities (i) real $\chi'(T)$ component and (ii) imaginary $\chi''(T)$ component of bulk polycrystalline Co$_2$SnO$_4$ system recorded at various frequencies under warming condition using dynamic magnetic field of amplitude $h_{ac} = 4$ Oe and zero static magnetic field $H_{dc} = 0$. The lines connecting the data points are visual guides [27].

Figure 7(b). The temperature dependence of the ac-magnetic susceptibilities (iii) real $\chi'(T)$ component and (iv) imaginary $\chi''(T)$ component of bulk polycrystalline Co$_2$TiO$_4$ system recorded at various frequencies under warming condition using dynamic magnetic-field of amplitude $h_{ac} = 4$ Oe and zero static magnetic field $H_{dc} = 0$. The lines connecting the data points are visual guides [33].
The least-square fit using the power law of the data shown in Figure 7 is depicted in Figure 8b. Here, $T_{SG}$ is the freezing temperature, $\tau_0$ is related to the relaxation of the individual cluster magnetic moment, and $z\nu$ is a critical exponent. The least-square fit analysis for Co$_2$SnO$_4$ gives $T_{SG} = 39.6$ K, $\tau_0 = 1.4 \times 10^{-15}$ s, and $z\nu = 6.4$. Since the value of $z\nu$ obtained in the present case lies well within the range (6–8) of a typical spin-glass systems; thus, one can conclude that Co$_2$SnO$_4$ exhibits spin-glass-like phase transition across 39 K just below the $T_N \sim 41$ K [20, 27]. In these studies, the difference in $T_\alpha$ and $T_{SG}$ is very small (~0.3 K) suggesting the close resemblance between the current Co$_2$SnO$_4$ system and the compounds exhibiting spin-glass-like transition. However, the situation for Co$_2$TiO$_4$ is bit different; in particular, the best fit to the Vogel-Fulcher law yields $T_\alpha = 45.8$ K and $\tau_0 = 3.2 \times 10^{-16}$ s and the power law yielded fairly unphysical values of the fitting parameters: for example, $\tau_0 \sim 10^{-33}$ s with $z\nu > 16$, indicating the lack of spin-glass-like phase transition [33]. Although, the magnitude and shift of the ac-susceptibility values both $\chi'(T)$ and $\chi''(T)$ strongly suppressed in the presence of dc-magnetic field ($H_{DC}$) in a similar way as it occurs in a typical spin-glass system perfectly following the linear behavior of $H^{bo}$ versus $T_f$ (AT-line analysis). Under such tricky situation, it is very difficult to conclude that Co$_2$TiO$_4$ is a perfect spin-glass or not (of course one can call it as a pseudo-spin-glass system). Nevertheless, the ac-magnetic susceptibility data and its analysis suggested that the both Co$_2$SnO$_4$ and Co$_2$TiO$_4$ systems consist of interacting magnetic clusters close to a spin-glass state.

Another interesting feature of both Co$_2$SnO$_4$ and Co$_2$TiO$_4$ is that they show asymmetry in M-H hysteresis loops unveiling giant coercivities and bipolar exchange bias under both ZFC and FC cases below their $T_N$ [27, 31, 33]. Earlier studies by Hubsch et al. have shown unusual temperature dependence of coercive field $H_C(T)$ in polycrystalline Co$_2$TiO$_4$ sample where the M-H loops were measured in 20-kOe field at different temperatures below 60 K [31]. It is well known that the discovery of exchange-bias ($H_{EB}$) effect in the structurally single-phase materials with mixed magnetic phases has recently gained tremendous attention because of its technological applications in the development of Read/Write heads of the magnetic

![Figure 8](https://www.nature.com/nmats/)

**Figure 8.** The best fit of the relaxation times to the (a) Vogel-Fulcher law and the (b) power law for the spinels Co$_2$SnO$_4$ and Co$_2$TiO$_4$. 
recording devices [41]. Generally, $H_{EB}$ has been experimentally observed only in the systems cooled in the presence of external magnetic field (FC mode) from above the Néel temperature or spin-glass freezing point. Such systems usually comprise of variety of interfaces such as ferromagnetic (FM)-antiferromagnetic (AFM), FM-SG, FM-ferrimagnetic, AFM-ferrimagnetic, and AFM-SG [41–49]. However, few recent papers have reported significant $H_{EB}$ even under the zero-field-cooled samples of bulk Ni-Mn-In alloys and in bulk Mn$_2$PtGa [48, 49]. The source of such unusual $H_{EB}$ under zero-field-cooled sample was attributed to the presence of complex magnetic interfaces such as ferrimagnetic/spin-glass or AFM/spin-glass phases [48–51]. Some recent reports have suggested that large exchange anisotropy can originate from the exchange interaction between the compensated host and ferromagnetic clusters [48–51]. Strikingly, Hubsch et al. observed the $H_{EB} \rightarrow 0$ anomalies across $T_{CMF}$, $T_{SG}$, and $T_N$ in the temperature-dependent data of $H_c$ for Co$_2$TiO$_4$ samples [31]. Slightly different results were reported by Nayak et al. in Ref. [33], where $H_c$ values drops monotonically on approaching $T_N$. However, the behavior of temperature dependence of exchange-bias field $H_{EB}(T)$ and remanent magnetization $M_R(T)$ in Ref. [33] closely resembles with the trend of $H_c(T)$ reported by Hubsch et al. in polycrystalline Co$_2$TiO$_4$ samples. On the other hand, the temperature behavior of $H_{EB}(T)$, $H_c(T)$, and $M_R(T)$ in Co$_2$SnO$_4$ is way different from that of Co$_2$TiO$_4$ though they are isostructural with each other. It is likely that the different magnitudes and different temperature dependences of the moments on the Co$^{2+}$ ions on the “A”- and “B”-sites in Co$_2$SnO$_4$ are responsible for the anomalous behavior in the $H_{EB}(T)$, $H_c(T)$, and $M_R(T)$ observed below $T_N$. Moreover, in Co$_2$SnO$_4$ below about 15 K, the data suggest that there is nearly complete effective balance of the antiferromagnetically coupled Co$^{2+}$ moments at the“A”- and”B”-sites leading to negligible values of $H_c$ and $M_R$.

Results from neutron diffraction in Co$_2$TiO$_4$ suggested the presence of canted-spins, likely resulting from magnetic frustration caused by the presence of nonmagnetic Ti$^{4+}$ ions on the”B”-sites. A similar canting of the spins might be present in Co$_2$SnO$_4$, although neutron diffraction studies are needed to verify this suggestion [27, 31, 33]. Other Co-based spinel compounds that display the reversal in the orientation of the magnetic moments along with negative magnetization due to the magnetic-compensation phenomena are CoCr$_2$O$_4$ and Co(Cr$_{0.95}$Fe$_{0.05}$)$_2$O$_4$ [3, 52, 53].

4. Magnetic properties of bulk and nanocrystalline Co$_2$MnO$_4$

Among various Co$_2$XO$_4$ (X = Mn, Ni, Co, Zn, etc.) spinels, Co$_2$MnO$_4$ has retained a unique place. In particular, Mn- and Co-based spinel oxides have gained considerable interest in the recent past due to their numerous applications in the Li-ion batteries [54, 55], sensors [56–58], thermistors [59], energy-conversion devices [60], and as a catalyst for the reduction of nitrogen oxides [61]. Moreover, Co$_2$MnO$_4$ nanocrystals have demonstrated outstanding catalytic properties for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) [60]. ORR and OER are the essential reactions in the electrochemistry-based energy-storage and energy-conversion devices. Co$_2$MnO$_4$ has shown superior catalytic activities compared to the commercial 30 wt% platinum supported on carbon black (Pt/C). Due to the special surface
Co$_2$MnO$_4$ spinel is a very promising pseudo-capacitor material [63, 64]. Co$_2$MnO$_4$ has also demonstrated potential applications for protective coating on ferrite stainless steel interconnects in solid-oxide fuel cells (SOFCs) [65, 66]. Furthermore, colossal magnetoresistance (CMR) has been observed in the Mn- and Co-based spinel oxides [67].

In addition to the novel catalytic properties, Co$_2$MnO$_4$ spinel exhibits intriguing magnetic properties. Lotgering first observed the existence of ferromagnetic ordering in Co$_2$MnO$_4$ spinels [68]. Ríos et al. systematically studied the effect of Mn concentration on the magnetic properties of Co$_{3-x}$Mn$_x$O$_4$ solid solutions prepared by spray pyrolysis [69]. As we have discussed in Section 2 that Co$_3$O$_4$ has an antiferromagnetic order with $T_N = 30$ K. When we replace Co in Co$_3$O$_4$ by Mn cation, large ferromagnetic ordering appears, which ultimately dominates the antiferromagnetic ordering at $x = 1$. Therefore, pure Co$_2$MnO$_4$ shows ferromagnetic behavior and this has been confirmed by detailed magnetic measurements [70, 71]. However, for value of $x$ other than 0 (Co$_3$O$_4$) and 1 (Co$_2$MnO$_4$), both ferromagnetic and antiferromagnetic magnetic exchange interactions coexist in the system, which yields a ferrimagnetic ordering in the Co$_{3-x}$Mn$_x$O$_4$ ($0 < x < 1$) solid solutions [72]. Tamura performed pressure-dependent study of Curie temperature ($T_C$) and found that $T_C$ decreases with increase in pressure [71].

Pure Co$_2$MnO$_4$ possess a cubic inverse-spinel structure: (B$^{3+}$)[A$^{2+}$B$^{3+}$]O$_4$ (shown in Figure 9). In an ideal case, the octahedral [B] sites are occupied by divalent cations together with half of the trivalent cations and the rest of the trivalent cations occupy the tetrahedral (A) sites in the spinel structure. However, due to the presence of different oxidation states of Mn and Co cations at (A) and [B] sites, the actual cationic distribution of Co$_2$MnO$_4$ is very complex and it has been a topic of considerable debate [59, 70–84]. Different sample preparation conditions also play an important role in the cationic distribution of Co$_2$MnO$_4$. On the basis of X-ray diffraction, electrical conductivity, magnetic, physiochemical, and neutron diffraction measurements, several different cationic distributions for nonstoichiometric Co$_{3-x}$Mn$_x$O$_4$ systems obtained after the thermal decomposition of co-precipitated manganese and cobalt salts [72]. Later studies by Blasse suggested a different cationic distribution: Co$^{2+}$[Co$^{3+}$Mn$^{3+}$]$^2_0$.08[Mn$^{4+}$]$^2_0.06$O$_4$ for Co$_2$MnO$_4$ powder samples prepared by thermal decomposition of nitrate salts [74]. From the neutron diffraction and magnetic measurements, Boucher et al. reported the cationic distribution Co$^{2+}$[Co$^{3+}$Mn$^{3+}$]$^2_0$.35[Mn$^{4+}$]$^2_0.36$O$_4$ similar to the one reported by Wickham and Croft [72, 75]. Yamamoto et al. [76] performed neutron diffraction measurements on Co$_2$MnO$_4$ oxides prepared by chemical methods at low temperatures, and reported Mn$_{0.8}$Co$_{0.2}$Mn$_{0.35}$Co$_{0.29}$O$_4$ as atomic distribution. Here, $n$ is the inversion parameter of the inverse-spinel structure. Gautier et al. suggested two different possible cationic distributions: Co$^{2+}$[Co$^{3+}$Mn$^{2+}$]$^2_0$.25[Mn$^{3+}$]$^2_0.36$O$_4$ and
Co$^{2+}$[Co$^{2+}$Mn$^{2+}$]$_{0.95}$Mn$^{3+}_{0.015}$Mn$^{4+}_{0.50}$O$_4$] [77, 78]. On the contrary, the electrical conductivity measurements suggest a different cationic distribution: Co$^{2+}$[Co$^{2+}$]$^{x}$Mn$^{4+}$]$_{1−x}$O$_4$, and Co$^{2+}$[Co$^{2+}$Mn$^{4+}$]O$_4$ or Co$^{3+}$[Co$^{3+}$Mn$^{2+}$]O$_4$ [59, 79] for Co$_3$MnO$_4$ spinel. Aoki studied the phase diagram and cationic distribution of various compositions of manganese and cobalt mixed spinel oxides [80]. He further investigated the effect of temperature and Mn concentration on the structure of manganese-cobalt spinel oxide systems. Control over morphology, crystallite site, grain size, and specific surface area of Co$_3$MnO$_4$ powders can be achieved by thermal decomposition of precursors in a controlled atmosphere [81, 82].

Figure 9. Cubic inverse-spinel structure of Co$_3$MnO$_4$ in Fd-3m (227) space group.

In 2008, Bazuev et al. investigated the effect of oxygen stoichiometry on the magnetic properties of Co$_2$MnO$_{4+δ}$ [83]. Accordingly, two oxygen-rich compositions, (i) Co$_2$MnO$_{4.62}$ and (ii) Co$_2$MnO$_{4.275}$, were prepared by the thermal decomposition of presynthesized Co and Mn binary oxalates (Mn$_{1/3}$Co$_{2/3}$C$_2$O$_4$·2H$_2$O). Above studies also report existence of anomalous behavior in the magnetic properties of Co$_2$MnO$_{4+δ}$ spinel at low temperatures and high magnetocrystalline anisotropy in Co$_2$MnO$_{4.62}$. Bazuev et al. also noticed that $T_N$ of Co$_2$MnO$_{4+δ}$ is highly sensitive to the oxygen stoichiometry, imperfections in the cationic sublattice and variation in the Mn oxidation states. The imperfect Co$_2$MnO$_{4+δ}$ inherits ferrimagnetic ordering that arises due to the antiferromagnetic exchange between Co$^{2+}$ ($e^4_{g}g^2_{2g}$) and Mn$^{4+}$ ($e^3_{2g}g^0_{2g}$) cations located at the tetrahedral and octahedral sites, respectively. To further investigate the electronic states of Mn and Co cations in the Co$_2$MnO$_4$ lattice, Bazuev et al. employed the X-ray absorption near-edge spectroscopy (XANES) to probe the electronic states of the absorbing atoms and their local neighborhood [83]. XANES spectra of both Co$_2$MnO$_{4.62}$ and Co$_2$MnO$_{4.275}$ compositions revealed that Co is present in both Co$^{2+}$ and Co$^{3+}$ oxidation states while Mn is present as Mn$^{4+}$ and Mn$^{3+}$. Additionally, it was found that Mn is located in a higher symmetry octahedral crystal field environment [83]. Bazuev et al. further proposed following cationic
distributions for Co$_2$MnO$_4$ and Co$_2$MnO$_4$ compositions: Co$_{0.936}^{2+}$[Co$_{0.936}^{III}$Mn$_{0.421}^{III}$]$_{0.515}$O$_4$ and Co$_{0.66}^{2+}$[Mn$_{0.866}^{IV}$Co$_{1.072}^{III}$]O$_4$, respectively. Here, Co$^{III}$ is a low-spin cation while Co$^{2+}$ and Mn$^{3+}$ are high-spin cations.

Co$_2$MnO$_4$ spinels have gained peculiar interest of researchers due to their unusual magnetic hysteresis behavior at low temperatures. Joy and Date [70] first observed the unusual magnetic hysteresis behavior in Co$_2$MnO$_4$ nanoparticles below 120 K. By means of the magnetic hysteresis loop measurements at low temperatures, they realized that the initial magnetization curve (virgin curve) lies outside the main hysteresis loop at 120 K. However, for $T > 120$ K, they observed normal hysteresis behavior in Co$_2$MnO$_4$. This unusual behavior of hysteresis loop at low temperatures can be associated with the irreversible domain wall motion. At low magnetic fields ($H < H_c$), domain walls experience substantial resistance during their motion with increasing magnetic field. Similar behavior has been observed for some other alloys [85–87]. Such irreversible movement of domain walls was ascribed to the rearrangement of valence electrons at low temperatures. Generally, in a system with mixed oxidation states of Mn at high temperatures, short-range diffusion of Co ions, Co$^{3+} \rightleftharpoons$ Co$^{2+}$ associated with Mn$^{3+} \rightleftharpoons$ Mn$^{4+}$, gets activated at low temperatures. This may cause change in the local ordering of the ions at the octahedral sites. Consequently, the resistance for domain wall motion increases and this slows down the motion of domain walls. Soon after Joy and Date, Borges et al. [84] confirmed that the unusual hysteresis of Co$_2$MnO$_4$ compound indeed arises due to the irreversible domain wall motion. Borges et al. prepared various different size nanoparticles of Co$_2$MnO$_4$ by Pechini method and performed the magnetic hysteresis measurements at low temperatures [84]. They observed that the samples below a critical diameter ($d < 39$ nm) exhibit normal hysteresis behavior, while the bulk grain size samples ($d \sim 200$ nm) show unusual hysteresis behavior at low temperatures. Using the spherical particle model, Borges et al. further calculated the critical diameter ($d_{cr}$) of a single-domain wall in Co$_2$MnO$_4$ and obtained that $d_{cr} = 39$ nm [88]. Therefore, all particles with diameter $d < d_{cr}$ can be considered as a single-domain particle. Since particles with $d < d_{cr}$ show normal hysteresis while particles with $d > d_{cr}$ show unusual hysteresis behavior, one can conclude that the unusual hysteresis behavior is indeed due to the irreversible motion of the domain walls.

The dynamic magnetic properties of Co$_2$MnO$_4$ nanoparticles of average diameter 28 nm were reported by Thota et al. [89]. A detailed study of dc- and ac-magnetic susceptibility measurements of these nanoparticles reveals the low temperature spin-glass-like characteristics together with the memory and aging effects (Figure 10). Figure 10 shows the temperature dependence of real and imaginary part of the ac-susceptibility ($\chi'(T)$ and $\chi''(T)$) of Co$_2$MnO$_4$ nanoparticles recorded at different values of frequencies ($f$) between 1 Hz and 1.48 kHz at a peak-to-peak amplitude of 1 Oe. Both $\chi'(T)$ and $\chi''(T)$ exhibit a sharp peak at the onset of ferromagnetic ordering ($T_C = T_1 \approx 176.4$ K) and a broad cusp centered at $T_2 (< T_C)$.

The temperature at which both $\chi'(T)$ and $\chi''(T)$ attain the maximum value shifts toward high-temperature side as the frequency increases from 1 Hz and 1.48 kHz similar to spin-glass behavior. Such frequency dependence of $\chi'(T)$ and $\chi''(T)$ follows the Vogel-Fulcher law (Eq. (4) and insets of Figures 10a(ii) and b(ii)) and power law of critical slowing down (Eq. (5) and
insets of Figures 10a(i) and b(i)). Least-square fit to these equation yields the following parameters (insets of Figure 10): interparticle interaction strength ($T_0$) = 162 K for $T_1$ (118 K for $T_2$) and relaxation time constant $\tau_0 = 6.18 \times 10^{-15}$ s for $T_1$ ($4.4 \times 10^{-15}$ s for $T_2$), critical exponent $(z\nu) = 6.01$ for $T_1$ (7.14 for $T_2$), and spin-glass transition temperature ($T_{SG}$) = 162.6 K for $T_1$ (119.85 K for $T_2$). Since the values of $z\nu$ for both the peaks $T_1$ and $T_2$ of Co$_2$MnO$_4$ nanoparticles lie well within the range (6–8) of a typical spin-glass systems, one can conclude that Co$_2$MnO$_4$ exhibits spin-glass-like phase transition across 162.6 K just below the $T_C \sim 176.4$ K [89]. Figure 11a shows the magnetization relaxation of Co$_2$MnO$_4$ nanoparticles under ZFC and FC protocols with a temperature quench to 70 K at $H = 250$ Oe [89]. The magnetization relaxation during the third cycle appears as a continuation of first cycle (Figures 11b and c). Relaxation of ZFC magnetization with temperature quenching confirms the existence of memory effects in Co$_2$MnO$_4$ nanoparticles. A noticeable wait-time ($t_{wt}$) dependence of magnetization relaxation (aging) at 50 K in both $M_{ZFC}$ and $M_{FC}$ was noticed in these Co$_2$MnO$_4$ nanoparticles, which further supports the presence of the spin-glass behavior observed in this system.

Figure 10. The real and imaginary components of the ac-magnetic susceptibilities ($\chi'(T)$ and $\chi''(T)$) of Co$_2$MnO$_4$ nanoparticles measured at various frequencies. The insets a(i) and b(i) represent the Vogel-Fulcher law whereas the insets a(ii) and b(ii) represent the power law of critical slowing down for both the peaks $T_1$ and $T_2$.
Figure 11. Magnetization relaxation $M(t)$ under ZFC and FC protocols with a temperature quench to 70 K at $H = 250$ Oe. The continuation of the first and third relaxation process during (b) ZFC and (c) FC cycles.

The high-temperature inverse magnetic susceptibility ($1/\chi_{ZFC}$ versus $T$) data of Co$_2$MnO$_4$ nanoparticles (Figure 12) fit well with the Néel’s expression for ferrimagnets:

$$
\frac{1}{\chi} = \frac{T}{C} + \frac{1}{\chi_0} \left[ \frac{\sigma_0}{T - \theta} \right]
$$

Figure 12. The scattered data represent the high-temperature inverse magnetic susceptibility ($1/\chi_{ZFC}$ versus $T$) of Co$_2$MnO$_4$ nanoparticles and the solid line represents the best fit to the Néel’s expression for ferrimagnets Eq (6).
The fit (red line in Figure 12) yields: $C = 0.0349 \text{ emu K/g Oe}$, $\chi_0 = 4.5 \times 10^{-5} \text{ emu/g Oe}$, $\sigma_0 = 5.76 \times 10^4 \text{ g Oe K/emu}$, $\theta = 169.8 \text{ K}$, and the asymptotic Curie temperature $T_a = C/\chi_0 = 775.6 \text{ K}$ [90, 91]. $T_a$ gives us information about the strength of antiferromagnetic exchange coupling between Mn$^{3+}$ and Mn$^{4+}$ at octahedral sites. Moreover, the effective magnetic moment $\mu_{\text{eff}}$ calculated using expression: $C = \frac{N\mu_{\text{eff}}^2}{3k_B}$ turns out to be $8.13 \mu_B$.

5. Concluding remarks

In this review, magnetic properties of bulk and nanoparticles of the Co-based spinels Co$_3$O$_4$, Co$_2$SnO$_4$, Co$_2$TiO$_4$, and Co$_2$MnO$_4$ have been summarized. The fact that the observed magnetic properties of these spinels are so different is shown to result from the different occupation of the cations on the A- and B-sites and their different electronic states at these sites. The richness of the properties of spinels thus results from these differences.

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References


