Antisite disorder driven spontaneous exchange bias effect in La$_{2-x}$Sr$_x$CoMnO$_6$ ($0 \leq x \leq 1$)

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Abstract
Doping at the rare-earth site by divalent alkaline-earth ions in perovskite lattice has witnessed a variety of magnetic and electronic orders with spatially correlated charge, spin and orbital degrees of freedom. Here, we report an antisite disorder driven spontaneous exchange bias effect as a result of hole carrier (Sr$^{2+}$) doping in La$_{2-x}$Sr$_x$CoMnO$_6$ ($0 < x < 1$) double perovskites. X-ray diffraction and Raman spectroscopy have evidenced an increase in disorder with the increase of Sr content up to $x = 0.5$ and thereby a decrease from $x = 0.5$ to 1. X-ray absorption spectroscopy has revealed that only Co is present in the mixed valence of Co$^{2+}$ and Co$^{3+}$ states with Sr doping to compensate the charge neutrality. Magnetotransport is strongly correlated with the increase of antisite disorder. The antisite disorder at the B-site interrupts the long-range ferromagnetic order by introducing various magnetic interactions and instigates reentrant glassy dynamics, phase separation and canted type antiferromagnetic behavior with the decrease of temperature. This leads to a novel magnetic microstructure with unidirectional anisotropy that causes a spontaneous exchange bias effect that can be tuned with the amount of antisite disorder.

Keywords: double perovskites, antisite disorder, spontaneous exchange bias

(Some figures may appear in colour only in the online journal)

1. Introduction

Strong interplay among the charge, lattice, orbital and spin degrees of freedom in perovskite materials (ABO$_3$, A-rare-earth and B-transition metal ions) induces distinct, fascinating, complex and rich physical phenomena such as metal–insulator transition, colossal magnetoresistance, superconductivity, charge/orbital ordering and multiferroicity [1–7]. One of the straightforward experimental methods for tuning these extraordinary physical properties is by doping at the A-site (with cations of different charge/radii). The quenched disorder with local distortion arising from the difference in ionic radii at the A-site cation and/or random Columbic potentials with the multiple valence states [8] is a provoking agent for the suppression of ordering parameters like magnetism, charge ordering and superconductivity [9–11], however, it induces interesting properties such as multiglass behavior, phase separation, ferroelectricity and the exchange bias (EB) effect [12–15]. The energy balance between the competing phases leads to phase coexistence at submicron length scales and induces meta-magnetic/electric phase transitions [16, 17]. Double perovskite La$_2$(Co/Ni)MnO$_6$ systems have attracted considerable interest in recent years due to their magnetodielectric (MD) effect and possible applications in spintronics. Structural and magnetic studies have demonstrated the long-range FM ordering that originates from the superexchange
interaction between (Co/Ni)$^{2+}$ and Mn$^{4+}$ magnetic species arranged with the rock-salt configuration at the B-sublattice of the perovskite cell. However, the existence of antisite disorder (ASD) is inevitable in the double perovskite structure and plays a vital role in their physical properties. In FM/ferrimagnetic double perovskites, these ASD induced AFM exchange interactions are responsible for the magnetic frustration, phase separation and large magnetoresistance at low fields; further, they also reduce the saturation magnetization and destroy the half-metallicity [18, 19]. On the other hand, a large ME coupling over a broad temperature range was found in partially disordered La$_2$NiMnO$_6$ and such a disorder manifests a reentrant spin glass (RSG) behavior at low temperatures, while a fully ordered sample has shown feeble magnetoelectric effect [20, 21]. Contrastingly, a large MD was observed in the highly ordered isostructural La$_2$CoMnO$_6$ (LCMO) sample in single

Figure 1. (a) HRXRD pattern of all the Sr doped La$_{2-x}$Sr$_x$CoMnO$_6$ ($0 \leq x \leq 1$) series of samples, (b) magnified view of the XRD peak at $2\theta=32.5^\circ$ for all samples, and (c),(d) show the Rietveld refinement of the XRD pattern of $x=0$ and $x=0.5$ doped samples.

Table 1. The structural parameters of Sr doped La$_{2-x}$Sr$_x$CoMnO$_6$ ($0 \leq x \leq 1$) samples estimated from the Rietveld refinement.

<table>
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<tr>
<th>La$_{2-x}$Sr$_x$CoMnO$_6$</th>
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<th>$x=0.4$</th>
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<th>$x=0.75$</th>
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<td>Monoclinic +</td>
<td>Disordered</td>
<td>Disordered</td>
<td>Disordered</td>
<td>Disordered</td>
<td>Disordered</td>
</tr>
<tr>
<td></td>
<td></td>
<td>disordered</td>
<td>rhombohedra</td>
<td>rhombohedra</td>
<td>rhombohedra</td>
<td>rhombohedra + cubic</td>
<td>rhombohedra + cubic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P2_1/n$</td>
<td>$P2_1/n + R3c$</td>
<td>$R3c$</td>
<td>$R3c$</td>
<td>$R3c$</td>
<td>$R3c + Fm-3m$</td>
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<td>$a$ (Å):</td>
<td>5.5223</td>
<td>5.4812 + 5.5124</td>
<td>5.4969</td>
<td>5.4825</td>
<td>5.4717</td>
<td>5.4785 + 7.6857</td>
<td>5.467 + 7.6717</td>
</tr>
<tr>
<td>$b$ (Å):</td>
<td>5.4862</td>
<td>5.4776 + 5.5124</td>
<td>5.4969</td>
<td>5.4825</td>
<td>5.4717</td>
<td>5.4785 + 7.6857</td>
<td>5.467 + 7.6717</td>
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<tr>
<td>$\alpha$, $\beta$ and $\gamma$ (degree):</td>
<td>$\alpha = \beta = 90$ &amp; $\gamma = 120$</td>
<td>$\alpha = \beta = 90$ &amp; $\gamma = 120$</td>
<td>$\alpha = \beta = 90$ &amp; $\gamma = 120$</td>
<td>$\alpha = \beta = 90$ &amp; $\gamma = 120$ &amp; $\alpha = \beta = \gamma = 90$</td>
<td>$\gamma = 120$ &amp; $\alpha = \beta = \gamma = 90$</td>
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<td></td>
</tr>
<tr>
<td>Bond length</td>
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<td>1.9634</td>
<td>1.9527</td>
<td>1.9447</td>
<td>1.9409</td>
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<td>1.9509</td>
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</tr>
<tr>
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<td>1.4</td>
<td>1.2</td>
<td>1.3</td>
<td>1.2</td>
<td>1.840</td>
<td>2.6</td>
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crystals and polycrystalline forms, while relatively small MD response was reported in the disordered sample [22–24]. Interestingly, a divalent cation (Sr$^{2+}$) doping at the rare-earth site in La$_2$NiMnO$_6$ has led to the magnetic disorder and exhibited EB effect [25].

In magnetically phase separated systems, the EB effect is anticipated. EB is an interface magnetic coupling phenomena which is manifested as the hysteresis loop shift along the field axis after cooling the system under a magnetic field. The EB effect is ubiquitous to spintronic applications, hence, understanding and controlling this effect with the disorder is essential. Lately, there has been great interest in electrical field control of EB devices [26]. In certain systems below the blocking temperature a spontaneous loop shift can be observed without the assistance of external magnetic field in the cooling mode and this unusual zero-field-cooled (ZFC) $M(H)$ loop shift is called zero-field-cooled EB (ZEB) or spontaneous EB effect [27–29]. Such a spontaneous EB effect will be of great interest in the case of electric field control of EB devices as it eliminates the requirement of external magnetic field to create the unidirectional anisotropy. Recently, we have reported a giant value of spontaneous and conventional EB effects in the La$_{1.5}$Sr$_{0.5}$CoMnO$_6$ system [30]. Metamagnetic behavior and a field induced phase separation below canted antiferromagnetic (CAF) transition are found to be responsible for the observed giant values of ZEB and conventional exchange bias (CEB) effects. To unveil the reason behind the complex magnetic behavior and field induced unidirectional anisotropy in the phase separated region, we have investigated the effect of Sr doping on the EB phenomena. Our study signifies the spin disorder to order state with Sr doping and as a consequence of ASD, a novel magnetic interface is formed that sets the ZEB effect.

The paper is structured into the following sections: section 2 describes the details of various experiments employed to characterize the samples. Section 3 describes the preparation details of La$_{2-x}$Sr$_x$CoMnO$_6$ ($0 \leq x \leq 1$) samples, structural characterization by the x-ray diffraction (XRD), x-ray absorption spectra (XAS) and Raman studies. The effect of Sr induced disorder on magnetotransport behavior is detailed in section 4. Further, the temperature and magnetic field dependent dc and ac susceptibility studies are investigated and presented in a phase diagram in section 5. Finally in section 6 the importance of ASD is summarized.

2. Experimental details

Polycrystalline La$_{2-x}$Sr$_x$CoMnO$_6$ ($0 \leq x \leq 1$) bulk samples were prepared by the conventional sol-gel method and their synthesis details were given in [22]. Obtained precursor powder was calcinated at 1300 °C for 24h. Crystal structural analysis was done using high resolution x-ray diffraction (HRXRD) with Cu-Kα radiation. For the electronic structural study, we have carried out XAS of Co-$L_{2,3}$ and Mn-$L_{2,3}$ and Raman studies. The effect of Sr induced disorder on magnetotransport behavior is detailed in section 4. Further, the temperature and magnetic field dependent dc and ac susceptibility studies are investigated and presented in a phase diagram in section 5. Finally in section 6 the importance of ASD is summarized.

3. Synthesis and structural studies of La$_{2-x}$Sr$_x$CoMnO$_6$ ($0 \leq x \leq 1$) samples

3.1. Synthesis and crystal structural study

The XRD pattern of the La$_{2-x}$Sr$_x$CoMnO$_6$ (LSCMO) ($0 \leq x \leq 1$) series of samples is displayed in the figure 1(a). In
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Figure 3. Raman spectra of (a) La$_2$CoMnO$_6$ and (b) La$_2$-$_x$Sr$_x$CoMnO$_6$ (0 ≤ x ≤ 1) samples, and (c),(d) show the Sr content variation of Raman spectra and FWHM for $A_{1g}$ and $B_{1g}$ modes respectively.

3.2. X-ray absorption spectra

To confirm the valence states of Co and Mn, we have measured elemental and site specific x-ray absorption near edge spectra (XANES) and figures 2(a) and (b) show the room temperature normalized XANES measured in total electron yield (TEY) mode for the series of LSCMO samples. The valence state of Mn is compared with the reference spectra of MnO (Mn$^{2+}$), Mn$_2$O$_3$ (Mn$^{3+}$) and MnO$_2$ (Mn$^{4+}$) [31–33] as shown in figure 2(a). These spectral features of the Mn-L$_2$,3 edges of all the samples match well with that of MnO$_2$ spectra, which confirms the 4$^{+}$ valence state of Mn and is consistent with the unchanged bond length of Mn–O as obtained from XRD. For the Co case, in an undoped LCMO sample, as shown in figure 2(b), the observed peak position of the L$_3$ edge at 779.6 eV and the spectral shape matches well with that of CoO standard spectra [31] and this confirms the 2$^{+}$ valence state of Co. With Sr doping the Co$^{2+}$ peak is suppressed and the trivalent state of the Co (i.e. Co$^{3+}$) peak appears at ~780.8 eV and the observed XANES spectra for the x = 1 sample matches with that of Sr$_2$CoO$_3$Cl standard spectra, where Co resides in the 3$^{+}$ state [31, 34, 35]. From figure 2(b) it is clear that the valence state of cobalt ions increases with Sr doping from Co$^{2+}$ to Co$^{3+}$. In order to elucidate on the spin state of Co$^{3+}$ (either in high spin with 3d$^6$, S = 2 or low spin, 3d$^6$, S = 0), the spectra is compared with the XANES spectra of Sr$_2$CoO$_3$Cl for the high spin state and EuCoO$_3$ for the low spin state [31, 34]. The XANES of EuCoO$_3$ in the low spin
state is characterized by the main peak followed by a shoulder at higher energies in both the $L_2$- and $L_3$-edge. Contrastingly, in our Sr doped samples the shoulder is present at lower energies than the main peak in the $L_3$-edge and this is similar to the high spin state of Sr$_2$CoO$_3$Cl spectra [34].

3.3. Raman spectra study

Figures 3(a) and (b) show the room temperature Raman spectra of LCMO and La$_{2-x}$Sr$_x$CoMnO$_6$ ($0 < x \leq 1$) samples respectively. The observed Raman spectra are consistent with the previous reports where two peaks associated with the stretching mode ($A_{1g}$) and mixed mode $B_{1g}$ (anti-stretching and vibration) can be noticed [36, 37]. Sr doping changes the position, symmetric nature and intensity of both the peaks. Figures 3(c) and (d) show the variation of Raman shift of the two broad peaks at $A_{1g} \approx 645$ cm$^{-1}$ and $B_{1g} \approx 490$ cm$^{-1}$ with Sr doping and these values are obtained from the Lorentzian fit to the spectra. Here, the $A_{1g}$ peak shifts to the lower wavenumber side (softening) for $x = 0$–0.5, while it shifts towards the higher wavenumber side (hardening) for the $x = 0.6$–1.0 samples. On the other hand, the $B_{1g}$ mode shows exactly the opposite trend with Sr doping. Another important parameter obtained from the Raman spectra is full width at half maxima (FWHM), a measure of the phonon lifetime that in turn depends on the various factors such as: (i) disorder present in the system and (ii) biphasic crystal structure in the sample [36, 38]. We have plotted the variation of FWHM corresponding to both $A_{1g}$ and $B_{1g}$ modes with Sr content as shown in figures 3(c) and (d) respectively. Here, with the increase of Sr doping FWHM is found to be maximum for $x = 0.5$. This is consistent with the structural data.

4. Temperature and magnetic field dependent transport behavior

Figure 4(a) shows the temperature-dependent electrical resistivity ($\rho$) of Sr doped La$_{2-x}$Sr$_x$CoMnO$_6$ ($x = 0, 0.1, 0.25, 0.4, 0.5, 0.6, 0.75$ and 1) samples. Here, all the compositions have exhibited semiconducting behavior, i.e. $d\rho/dT < 0$ and the resistivity of the samples decreases monotonically with the carrier doping [39–42]. However, there is no anomaly in resistivity near to magnetic ordering at $T_C$ that suggests the electron mobility of the system is controlled by thermal energy rather than magnetic ordering. The enhanced electrical conduction with doping can be explained based on the new conduction path of Co$^{3+}$–O$^{2-}$–Mn$^{4+}$ within the matrix of the super-exchange interactions among the various magnetic species [43]. A large magnetoresistance (MR) of ~31% was reported in ordered parent LCMO single crystals and bulk samples [23, 44]. Though the origin of large MR is not well understood, an enhanced spin transport due to the alignment of neighboring transition metal ions with a magnetic field has been considered as a possible reason [44]. Temperature dependent MR of Sr = 0, 0.5 and 0.75 doped samples with 5 T field have shown negative MR that increases with the decrease of temperature and shows no anomaly near to magnetic ordering (not shown here). The isothermal magnetic field dependence of MR with Sr doping at 110 K is shown in figure 4(b). Here, a maximum MR of the parent LCMO is 34%, similar to the single crystal data, and this value increases to 51% for $x = 0.5$, and then decreases for $x \geq 0.6$. Such a non-monotonic variation of MR with Sr doping (as shown in the inset to figure 4(b)) suggests the strong correlation of magnetotransport with the magnetic disorder.

5. Magnetization study

5.1. Temperature dependent dc susceptibility

Temperature dependent magnetization of La$_{2-x}$Sr$_x$CoMnO$_6$ ($x = 0, 0.1, 0.25, 0.5, 0.75$ and 1) samples in zero-field cooled (ZFC) and field-cooled warming (FCW) modes for 100 Oe dc field is shown in figures 5(a)–(f). Here, the parent compound shows a single magnetic transition at ~230 K and it has been assigned to the Co$^{2+}$–O$^{2-}$–Mn$^{4+}$ FM superexchange interactions [36, 45]. With Sr doping from $x = 0.1$–0.4, in addition to the high-temperature FM phase ($T_{C1}$) another dominant magnetic ordering at $T_{C2}$ can be observed. This second magnetic transition can be attributed to Co$^{3+}$–O$^{2-}$–Mn$^{4+}$ FM superexchange interactions [30]. Further, the magnetic anomaly around 90–105 K in both FCC and ZFC magnetization has
been assigned to a glassy-like behavior and will be discussed later. At temperatures around 40–50 K depending on the Sr doping level (x = 0.1–0.75) a phase separation (PS) state containing FM and glassy phases can be noticed and further below, a CAF phase is established [30]. The PS temperature (T_{PS} (K)) is estimated from the first derivative of \( M \) with respect to temperature as shown in the inset of figures 5(b)–(f).

For doping \( x > 0.5 \), the magnetic glass anomaly is suppressed while the FM interactions corresponding to Co^{3+}–O^{2−}–Mn^{4+} are enhanced. Correspondingly, the PS state is shifted to low temperature (~10–15 K) in \( x = 0.75 \) and vanishes for the \( x = 1 \) sample. Further, one can note that the magnitude of the magnetization decreases with the increase of Sr doping. From figure 5, it is found that the magnetic irreversibility temperature (\( T_{irr} \)) (i.e. bifurcation in between FCC and ZFC magnetization) coincides with the paramagnetic (PM) to FM transition in \( x = 0–0.5 \) samples. Such a bifurcation in \( x = 0.1–0.5 \) can be attributed to frustration leading to the glassy phase. While for \( x > 0.5 \), \( T_{irr} \) is present even at temperatures well above the magnetic ordering (\( T_{C2} \)), and this suggests the presence of short-range FM interactions [46].

5.2. Temperature and frequency dependent ac susceptibility

Figures 6(a)–(f) and 7(a)–(f) show the temperature dependent in-phase component (\( \chi' \)) and out-of-phase component (\( \chi'' \)) of ac susceptibility respectively for the Sr(\( x \)) = 0, 0.1, 0.25, 0.5, 0.75 and 1.0 doped samples. In LCMO the frequency independent peak in \( \chi'(T) \) and \( \chi''(T) \) corresponds to the FM transition. In the doped samples, observed multiple peaks at \( T_{C1} \) and \( T_{C2} \) also show a frequency independent nature consistent with FM transition. The variation of \( T_{C1}, T_{C2} \) (obtained from the ac susceptibility data), and \( T_{p} \) and \( T_{CAF} \) (obtained from \( M \) data) with Sr doping are listed in table 2. A clear frequency dependence of the peak and its maximum value of \( \chi''(T) \) (freezing temperature \( T_{f} \)) at ~95–105 K in doped samples and its shift to higher temperature with the increase of frequency suggests the reentrant glassy dynamics. However, ac susceptibility shows no signature of CAF ordering at low temperatures. As shown in the inset of figures 7(b)–(e), in doped samples, a shift of \( T_{f} \) with relaxation time (\( \tau \)) has been analyzed by the critical slowing down power law [30, 47, 48]. The \( T_{f} \) versus \( \tau \) data fits well to the power law \( \tau = \tau_{0}(T_{f} - T_{f}^{0})^{-\nu} \) as shown in the inset of figures 7(b)–(e), where \( \tau_{0} \) is the microscopic spin relaxation time, \( T_{f}^{0} \) is glassy freezing temperature and \( \nu \) denotes the critical exponent. From the fitting, the obtained \( T_{f}, \tau_{0} \) and \( \nu \) values with Sr are listed in table 3. The high \( \tau_{0} \) (~10^{-6}–10^{-7} s) and small \( \nu \) (3–6) values in the case of \( x = 0.1–0.4 \) indicates the freezing of magnetic clusters rather than the individual atomic spins, suggesting the presence of cluster glass (CG)-like behavior. In the case of the \( x = 0.5 \) sample, \( \tau_{0} \) ~ 4.23 × 10^{-11} s and \( \nu = 10.34 \) reveal the RSG nature [30, 47]. Further, the double dip memory and aging effects are the characteristic
features of the spin glass (SG) phase and were confirmed in the $x = 0.5$ doped sample in our previous work [30].

Corroborating the dc and ac susceptibility measurements with structural data, a phase diagram for the La$_{2-x}$Sr$_x$CoMnO$_6$ ($0 \leq x \leq 1$) series of samples is shown in figure 8. It is clear that the magnetic glassy behavior in the temperature regime of ~50–110 K takes a sudden change from the CG ($x = 0.1$–0.4) to SG state at $x = 0.5$ where Co$^{2+}$ and Co$^{3+}$ are present in equal amounts. The various competing magnetic exchange interactions such as Co$^{2+}$–O$^{2-}$–Mn$^{4+}$ (FM), Co$^{3+}$–O$^{2-}$–Mn$^{4+}$ (FM), Co$^{3+}$–O$^{2-}$–Co$^{3+}$ (AFM) and Co$^{2+}$–O$^{2-}$–Co$^{2+}$ (AFM) with large magnetic ASD drive the system to the SG state [30, 49].

The complete absence of a glassy nature is realized for higher doping i.e. $x > 0.5$. And the end members will have all Co ions in either 2$^+$ state (for $x = 0$) or 3$^+$ state (for $x = 1$) and will have one defined FM ordering. This indicates that Sr doping induces spin disorder to order state in LCMO.

5.3. Isothermal field-dependent magnetization study

Figures 9(a)–(e) show the field variation of magnetization, $M(H)$ curves at 5 K for the selected samples ($x = 0, 0.25, 0.5, 0.75$ and 1) in two modes i.e. ZFC and field cooled with 5 T. Here, the parent compound ($x = 0$) exhibits a well-defined hysteresis loop with large remnant magnetization ($M_r$) and shows saturation-like behavior for fields $\geq 5$ T as depicted in figure 9(a). The obtained high magnetization ($M_S$) $\sim$ 5.75 $\mu_B$/f.u. at 6 T is close to the theoretically calculated spin only value of 6 $\mu_B$/f.u. as expected for the FM alignment of Co$^{2+}$–O$^{2-}$–Mn$^{4+}$ magnetic species [45].

From the figures 9(b)–(e), it is clear that Sr doping shows a significant effect on the shape of the hysteresis loop and magnetization value. Figure 9(f) shows the Sr content variation of $M_S$ obtained at 6 T, $M_r$ and coercive field ($H_C$) values at 5 K. Both $M_S$ and $M_r$ decrease with increasing Sr up to $x = 0.5$ and then show an increasing trend for $x > 0.5$, while $H_C$ variation with Sr doping shows the opposite trend and is consistent with the variation in magnetic disorder. With Sr doping the magnetization value decreases and reaches the lowest for $x = 0.5$ and beyond this the doping magnetization property improves. A large value of $H_C$ and low values of $M_r$ and $M_S$ at 5 K in the $x = 0.5$ sample supports the presence of more magnetic disorder. Here, we estimated ASD, which is the main cause for the reduction in $M_S$ values, by using [50],

$$M_S = (1−2\text{ASD}) \left[ M_{Co} + M_{Mn} \right] + x(2\text{ASD} − 1).$$

Figure 6. (a)–(f) Temperature dependent $\chi'$ with different frequencies of 1 Oe ac signal for Sr doped La$_{2-x}$Sr$_x$CoMnO$_6$ (Sr = 0, 0.1, 0.25, 0.5, 0.75 and 1.0) samples.

Figure 7. (a)–(f) Temperature dependent $\chi''$ with different frequencies for Sr doped La$_{2-x}$Sr$_x$CoMnO$_6$ ($x = 0, 0.1, 0.25, 0.5, 0.75$ and $1.0$) samples and the inset to their respective figures shows power law fit to experimental data of $T_f$ versus $\tau$ data.

Table 2. High temperature FM ($T_{C1}$) and low temperature FM ($T_{C2}$) ordering, magnetic glassy ($T_g$), PS temperature ($T_p$) and canted AFM ($T_{CAF}$) for Sr doped La$_{2-x}$Sr$_x$CoMnO$_6$ ($0 \leq x \leq 1$) samples.

<table>
<thead>
<tr>
<th>La$_{2-x}$Sr$_x$CoMnO$_6$</th>
<th>$T_{C1}$ (K)</th>
<th>$T_{C2}$ (K)</th>
<th>$T_g$ (K)</th>
<th>$T_p$ (K)</th>
<th>$T_{CAF}$ (K)</th>
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<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
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<td>$x = 0.25$</td>
<td>215</td>
<td>152</td>
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<td>45</td>
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<tr>
<td>$x = 0.4$</td>
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<tr>
<td>$x = 0.5$</td>
<td>—</td>
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<tr>
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<td>—</td>
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<tr>
<td>$x = 0.75$</td>
<td>—</td>
<td>153</td>
<td>—</td>
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<td>10</td>
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<tr>
<td>$x = 1.0$</td>
<td>—</td>
<td>175</td>
<td>—</td>
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</table>

Table 3. List of fitting parameters: freezing temperature ($T_g$), relaxation time ($\tau$) and critical exponent ($z\nu$) for the Sr doped La$_{2-x}$Sr$_x$CoMnO$_6$ ($0.1 \leq x \leq 0.5$) samples.

<table>
<thead>
<tr>
<th>La$_{2-x}$Sr$_x$CoMnO$_6$</th>
<th>$T_g$ (K)</th>
<th>$\tau_0$ (s)</th>
<th>$z\nu$</th>
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<td>94.77</td>
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<td>90.13</td>
<td>$4.23 \times 10^{-11}$</td>
<td>10.03</td>
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</tbody>
</table>

Figure 8. Phase diagram of La$_{2-x}$Sr$_x$CoMnO$_6$ ($0 \leq x \leq 1$) samples with Sr doping (FM-$T_{C1}$ and $T_{C2}$ are obtained from the frequency independent peak in $\chi''$-$T$ data and glassy freezing ($T_g$) from the frequency dependent peak in $\chi''$-$T$ data, while the phase separation temperature ($T_{PS}$) and canted antiferromagnetic temperature ($T_{CAF}$) are estimated from the first derivative of $M_{ZFC}$ with respect to temperature).
Here, $x$ denotes the amount of Sr doping and $M_{\text{Co}}$ and $M_{\text{Mn}}$ are the theoretically calculated spin only magnetic moments of Co and Mn ions respectively. In this expression, the first term indicates the contribution of ASD and the second term suggests the reduction in $M_{S}$ due to hole-carrier doping. Accordingly, we have calculated % of ASD with Sr variation and it is plotted in figure 9(f). Maximum ASD is found in $x = 0.5$ and it matches well with the structural, Raman and magnetotransport data. Here, $M_{S}$ has shown an almost linear dependence with ASD.

5.4. ZEB and CEB effects in La$_{2-x}$Sr$_{x}$CoMnO$_{6}$ samples

A definite $M(H)$ loop shift at 5 K (as shown in figures 9(a)–(e)) in both ZFC and FC modes for doped samples indicates asymmetry in the hysteresis loop about the origin in ZFC as well as in FC modes and they illustrate the corresponding ZEB and CEB effects. In the parent sample, both of these effects are found to be absent. While Sr doped samples exhibited the ZEB effect for $x = 0.1$–0.75. This loop shift is enhanced further in cooling the samples under the FC mode and much higher EB shifts are obtained in the CEB effect. The loop asymmetry along the field axis and magnetization axis can be quantified as EB field ($H_{\text{EB}} = (|H_{C1}| - |H_{C2}|)/2$) and EB magnetization ($M_{\text{EB}} = |M_{r1}| - |M_{r2}|)/2$) respectively. Here, $H_{C1}$ and $H_{C2}$ are the positive and negative intercepts of the magnetization curve with field axis, and $M_{r1}$ and $M_{r2}$ are the positive and negative intercepts of the $M(H)$ curve with magnetization axis, respectively. Obtained values of the ZEB and CEB effects with Sr doping are shown in figure 10. Like the ZEB effect, CEB also increases with Sr content from $x = 0.1$–0.5, reaches maximum for $x = 0.5$ and then decreases for higher Sr.

From the $M(T)$ and $M(H)$ data it is clear that the coexistence of FM and CAF phases appears in La$_{2-x}$Sr$_{x}$CoMnO$_{6}$ samples for a broad range of Sr ($0 < x < 1$) doping. CAF and PS are important ingredients to obtain the ZEB effect [30]. At low temperatures, $< 10$ K, the field induced metamagnetic phase transition
from the CAF to FM phase is responsible for the exchange bias effect. With ZFC, the system undergoes CAF ordering at low temperature. During the initial magnetization curve, magnetic field strength higher than the critical field which depends on temperature induces the FM phase. With decreasing field (in the second cycle of the $M(H)$ loop), the field induced FM phase is kinetically arrested and coexists with the CAF matrix, which creates a large unidirectional anisotropy at their interface. In the FC case, there exist FM clusters even at $H = 0$ Oe below the CAF transition that lead to a giant CEB effect [30]. A close look reveals that below the CAF transition, the CEB is actually an enhanced effect of the ZEB. This explanation is valid for all other Sr doped samples where ZEB is present. A small CEB is observed in between the CAF and PS regions, the unidirectional anisotropy formed at the FM and SG interface is responsible for the CEB effect and this is in a way similar to the EB effect in the phase separated cobaltates and manganites [51].

Generally in phase separated systems, the observed EB effect can be explained qualitatively based on the Meiklejohn–Bean (MB) model [52]. According to this model under certain assumptions [51, 53], the amount of EB field from the hysteresis loop shift in inhomogeneous magnetic systems can be estimated as $H_{EB} = 2\sqrt{A_{AFM}K_{AFM}/M_{FM}}$. Here, $A_{AFM}$ and $K_{AFM}$ are the exchange stiffness and uniaxial anisotropy energy of the AFM phase respectively, $t_{FM}$ and $M_{FM}$ are the thickness and saturation magnetization of the FM layer respectively. In the present case, with Sr doping for $x = 0.1$ to $x = 0.5$, the volume fraction of the CAF phase increases and is responsible for the decreasing of $M_s$ values (as shown in figure 9(f)). Such low temperature CAF anisotropy and the coupling strength at FM/AFM is the possible origin for the increase of the EB effect in both ZFC and FC modes (figure 10) and correspondingly both the ZEB and CEB effects increase and become maximum for $x = 0.5$ with high ASD. Further, for higher doping of $x > 0.5$, the weakening of AFM correlations and the increase of the average size of FM clusters analogues to $t_{FM}$ and $M_{FM}$ can reduce the interface coupling strength and unidirectional anisotropy; consequently it decreases the resultant ZEB and CEB effects.

6. Conclusions

The crystal structure of $\text{La}_2-x\text{Sr}_x\text{CoMnO}_6$ is sensitive to Sr doping and Raman results suggest that the disorder increases with Sr doping and is maximum for $x = 0.5$; further doping leads towards the order state. We can summarize that hole doping increases the ASD and various AFM interactions that systematically destroy long range magnetic ordering and induce magnetic glass and the PS state with CAF ordering at low temperatures. Our results demonstrate the observation of such complex magnetic behavior in $\text{La}_{2-x}\text{Sr}_x\text{CoMnO}_6$ ($0 \leq x \leq 1$) samples and observed field induced novel-magnetic interface related ZEB phenomena. The study signifies the impact of ASD on the magnetic and transport properties and presents large values of ZEB, CEB and MR. Importantly, tuning of EB with ASD disorder can be a constructive approach for designing new materials for spintronic applications.

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