Coexistence of interacting ferromagnetic clusters and small antiferromagnetic clusters in La$_{0.5}$Ba$_{0.5}$CoO$_3$

Devendra Kumar and A Banerjee

UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore-452001, India
E-mail: deven@csr.res.in

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Abstract

We report detailed dc magnetization and linear and nonlinear ac susceptibility measurements on the hole doped disordered cobaltite La$_{0.5}$Ba$_{0.5}$CoO$_3$. Our results show that the magnetically ordered state of the system consists of coexisting non-ferromagnetic phases along with percolating ferromagnetic clusters. The percolating ferromagnetic clusters possibly start a magnetic ordering at the Curie temperature of $201.5(5)$ K. The non-ferromagnetic phases mainly consist of antiferromagnetic clusters with size smaller than the ferromagnetic clusters. Below the Curie temperature the system exhibits an irreversibility in the field cooled and zero field cooled magnetization and a frequency dependence in the peak of ac susceptibility. These dynamical features indicate the possible coexistence of spin-glass phase along with ferromagnetic clusters similar to La$_{1-x}$Sr$_x$CoO$_3$ ($x \geq 0.18$), but the absence of field divergence in the third harmonic of ac susceptibility and zero field cooled memory clearly rule out any such possibility. We argue that the spin-glass phase in La$_{1-x}$Sr$_x$CoO$_3$ ($x \geq 0.18$) is associated with the presence of incommensurate antiferromagnetic ordering in non-ferromagnetic phases, which is absent in La$_{0.5}$Ba$_{0.5}$CoO$_3$. Our analysis shows that the observed dynamical features in La$_{0.5}$Ba$_{0.5}$CoO$_3$ may be due to progressive thermal blocking of ferromagnetic clusters, which is further confirmed by Wohlfarth’s model of superparamagnetism. The frequency dependence of the peak of ac susceptibility obeys the Vogel–Fulcher law with $\tau_0 \approx 10^{-9}$ s. This together with the existence of an AT-line in $H$–$T$ space indicates the presence of significant inter-cluster interaction among these ferromagnetic clusters.

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

1. Introduction

The transition metal oxides, e.g. manganites, cuprates, and cobaltites, exhibit a complex phase diagram including the microscopically inhomogeneous electronic states due to interplay of various competitive electronic energies such as electron kinetic energy, electron–electron Coulomb repulsion, spin–spin, spin–orbit, and crystal field interactions [1, 2]. Of these oxides, the cobaltite LaCoO$_3$ exhibits a unique property of temperature and doping dependent spin state transition [3, 4]. The Co$^{3+}$ ion in LaCoO$_3$ can exist in a low spin (LS) state with configuration $t^6_{2g}e^0_g$ ($S = 0$), an intermediate spin (IS) state with configuration $t^5_{2g}e^1_g$ ($S = 1$), and a high spin (HS) state with configuration $t^4_{2g}e^2_g$ ($S = 2$). The LaCoO$_3$ have a charge transfer insulator type non-magnetic ground state with Co$^{3+}$ ion in the LS state; it starts showing magnetic moment above 30 K and exhibits a paramagnetic-like behavior above 100 K [5, 6]. This change in magnetic moment and behavior is attributed to the thermally driven spin state transition of the Co$^{3+}$ ion, but the nature of the transition—whether it is an LS–IS transition or LS–HS transition—is still not completely settled [4–11]. The hole doping of LaCoO$_3$ by replacing the trivalent La$^{3+}$ with divalent Sr$^{2+}$ or Ba$^{2+}$ generates Co$^{4+}$, and each of these Co$^{4+}$ transforms its six nearest Co$^{3+}$ neighbors
into the IS state by forming octahedrally shaped spin state polaron.

These polaron, $e_g$ electrons of Co$^{3+}$ are delocalized and are shared by Co$^{3+}$ and Co$^{4+}$ ions of the polaron, while $t_{2g}$ electrons of both the ions are localized and couple ferromagnetically via double exchange interaction. For small hole doping these isolated spin state polaron are stable within the non-ferromagnetic matrix. Additional hole doping enhances the number density of spin state polaron, and above a critical doping of $x = 0.04$ the enhanced polaron density causes a decay of polaronic state due to ferromagnetic (FM) interaction between the intra-polaronic Co$^{3+}$ ions at the cost of the antiferromagnetic (AFM) intra-polaronic interaction [15]. This, in turn, results in the formation of hole rich ferromagnetic spin clusters embedded in non-ferromagnetic insulating matrix. On further enhancing the hole doping, at a critical concentration ($x = 0.18$ for Sr$^{2+}$ and $x = 0.2$ for Ba$^{2+}$), the ferromagnetic-metallic clusters eventually percolate, giving rise to long range ferromagnetic ordering and metallic conductivity [16].

For La$_{1-x}$Sr$_x$Co$_3$O$_7$, a spin-glass state is observed below the critical doping concentration for percolation of ferromagnetic-metallic regions, and above this a ferromagnetic or a ferromagnetic-cluster state is reported [16, 17]. Detailed investigations of the ferromagnetic-cluster state of La$_{1-x}$Sr$_x$Co$_3$O$_7$ suggest the presence of spin or cluster-glass-like behavior even in the so called ferromagnetic or ferromagnetic-cluster state [18–22], and it has been argued that this behavior is due to coexistence of the spin-glass phase with percolating ferromagnetic clusters [18, 21]. The absence of the exchange bias effect in La$_{0.5}$Sr$_{0.5}$Co$_3$O$_7$ clearly indicates that the spin-glass-like phase is not present at the interface of ferromagnetic clusters and non-ferromagnetic matrix, but instead it probably coexists as small patches with the percolating backbone of ferromagnetic clusters [21].

The nature of the magnetic state in La$_{1-x}$Ba$_x$Co$_3$O$_7$ with Ba$^{2+}$ having a larger ionic radius than Sr$^{2+}$ (ionic radii of La$^{3+}$ = 1.216 Å, Ba$^{2+}$ = 1.47 Å, Sr$^{2+}$ = 1.31 Å) is less studied, and the early reports indicate the presence of a ferromagnetic-metallic ground state for $x > 0.2$ [16, 23]. The higher ionic radius of Ba$^{2+}$ (a) enhances the local randomness due to larger size mismatch between the Ba$^{2+}$ and La$^{3+}$ ions, and (b) reduces the overall distortion from ideal perovskite structure so the tolerance factor $(t)$ approaches unity. This enhancement in tolerance factor straightens the Co–O–Co bonds, which in turn increases the ferromagnetic coupling due to double exchange interaction between Co$^{3+}$ and Co$^{4+}$ ions. Furthermore, the Ba$^{2+}$ doping enhances the concentration of the Jahn–Teller (JT) active IS state because of lattice expansion, and the formation of I–I magnetopolarons is found to be most preferable in the insulating phase of Ba doped cobaltites [13, 24].

In this paper we present results of detailed dc magnetization and linear and nonlinear ac susceptibility measurements of La$_{0.5}$Ba$_{0.5}$Co$_3$O$_7$ with an aim to understand its magnetically ordered state. We find that the magnetically ordered state of La$_{0.5}$Ba$_{0.5}$Co$_3$O$_7$ consists of small antiferromagnetic clusters coexisting with the percolating backbone of ferromagnetic clusters. In contrast to La$_{0.5}$Sr$_{0.5}$Co$_3$O$_7$, no signatures of spin-glass phase have been observed in La$_{0.5}$Ba$_{0.5}$Co$_3$O$_7$. Our analysis suggests that the existence of spin-glass phase in hole doped LaCo$_3$ (above critical concentration) is associated with the presence of incommensurate antiferromagnetic ordering in the non-ferromagnetic phases, which in turn depends on the ion radii and doping levels of divalent ions. Furthermore, we show that the observed dynamic properties in La$_{0.5}$Ba$_{0.5}$Co$_3$O$_7$ originate from the progressive thermal blocking of interacting ferromagnetic clusters.

2. Experimental details

Polycrystalline La$_{0.5}$Ba$_{0.5}$Co$_3$O$_7$ samples are prepared by the pyrophoric method [25] using high purity (99.99%) La$_2$O$_3$, BaCoO$_3$, and Co(NO$_3$)$_2$6H$_2$O. The stoichiometric quantities of La$_2$O$_3$, BaCoO$_3$, and Co(NO$_3$)$_2$6H$_2$O are separately dissolved in dilute nitric acid and then these solutions are mixed with triethanolamine (TEA), keeping the pH highly acidic. The final solution is dried at 100 °C, which burns and yields a black powder that is pelletized and subsequently annealed at 1100 °C for 12 h. These samples are characterized by x-ray diffraction on a Bruker D8 Advance x-ray diffractometer using Cu Kα radiation. The dc magnetization measurements are made on a 14 T Quantum Design physical property measurement system–vibrating sample magnetometer and the low field ac susceptibility measurements are made on an ac susceptibility setup which is described in [26].

The x-ray diffraction data of La$_{0.5}$Ba$_{0.5}$Co$_3$O$_7$ are collected at room temperature and analyzed with Rietveld structural refinement using FULLPROF software [27]. Figure 1 shows the XRD data, the Rietveld fit profile, the Bragg positions, and the difference in experimental and model results. The Rietveld refinement show that the sample is single phase and crystallizes in simple cubic Pn$ar{3}$m structure with lattice constant $a = 3.8726(2)$ Å and unit cell volume $V = 58.078(4)$ Å$^3$. The unit cell volume in disordered cobaltites depends on the oxygen stoichiometry, and the comparison of our result with that of [28] suggests that the oxygen non-stoichiometry ($\delta$ in La$_{0.5}$Ba$_{0.5}$Co$_3$O$_{7+\delta}$) is much less than 0.05. The oxygen content is determined by iodometric titration, which gives $\delta = 0.00(2)$. The fluctuation in the average atomic concentration of La, Ba, and Co is probed by energy dispersive analysis of x-rays (EDAX) attached to an FEI Tecnai G2–20 transmission electron microscope. EDAX measurements at the step of 0.5 μm along a randomly chosen straight line of 5 μm length give a variation of less than 0.5% in the average atomic concentration, which is within the experimental uncertainty (~1%) of EDAX. This shows that the La and Ba are uniformly distributed in the sample. The average crystallite size of the sample is estimated from XRD data using the Scherrer formula, which gives around 85 nm.

3. Results and discussion

3.1. DC magnetization

3.1.1. Thermomagnetic irreversibility. Figure 2 shows the temperature variation of magnetization in field cooled (FC)
dependence, with a variation of 0 coefficients of fitting show a small but unsystematic field $T_{33}$, or anisotropic ferromagnetic state [34]. At low fields spin-glass [29], cluster-glass [30, 31], superparamagnetic [32, with a peak in ZFC magnetization indicates the presence of a coincidence. The bifurcation in FC–ZFC magnetization along of the ZFC peak. At 1 T, the FC and ZFC curves almost coincide. The bifurcation in FC–ZFC magnetization curves show a rapid increase in magnetization, which is indicative of a paramagnetic to ferromagnetic transition. On further lowering the temperature, the FC curve keeps evolving while the ZFC curve bifurcates with that of FC at the temperature $T_p$. On increasing the measuring field $T_w$ and $T_p$ decrease with an enhancement in broadening of the ZFC peak. At 1 T, the FC and ZFC curves almost coincide. The bifurcation in FC–ZFC magnetization along with a peak in ZFC magnetization indicates the presence of a spin-glass [29], cluster-glass [30, 31], superparamagnetic [32, 33], or anisotropic ferromagnetic state [34]. At low fields $T_p < T_{irr}$, and below $T_p$ the FC magnetization is not constant with temperature. This observation is not in agreement with that of canonical spin-glasses and suggests that the system is possibly in a cluster-glass, superparamagnetic, or ferromagnetic state. Similar observations have been made on the other relatively well studied half-doped disordered cobaltite La$_{0.5}$Sr$_{0.5}$CoO$_3$ [17, 20, 21].

The high temperature magnetization data ($T > 250$ K) fit well with the Curie–Weiss law, and for 0.08 T field cooling the Curie constant $C = 1.59(1)$ emu K mol$^{-1}$ Oe$^{-1}$ and the Weiss constant $\theta = 210(2)$ K. See the inset of figure 2. The coefficients of fitting show a small but unsystematic field dependence, with a variation of 0.08 emu K mol$^{-1}$ Oe$^{-1}$ in $C$ and 3 K in $\theta$ in the field range of 0.05–1.0 T. The Curie constant of 1.59(1) emu K mol$^{-1}$ Oe$^{-1}$ gives an effective value of paramagnetic moment $\mu_{eff} = 3.566(3)$ $\mu_B$/f.u., and the positive value of Weiss constant indicates the dominance of ferromagnetic correlations in the ordered state. Below 250 K, the inverse dc susceptibility exhibits a upward deviation from the Curie–Weiss law. A similar upward deviation from the Curie–Weiss law above $T_C$ has also been observed in La$_{1-x}$Sr$_x$CoO$_3$, and it was attributed to the existence of short range ferromagnetic correlations above $T_C$ [35].

### 3.1.2. Coexistence of ferromagnetic and non-ferromagnetic phases.

In figure 3(a) we show the magnetization versus field plot at 10, 40, 180, 190, 200, 210, and 220 K. At low temperatures, for example at 10 K, the magnetization exhibits a saturation-like behavior at high magnetic fields which is typical of a ferromagnet, but a careful observation of the data indicates the presence of a non-saturating magnetization along with the saturating ferromagnetic component. The presence of this non-saturating component prohibits the magnetization from saturating even at high magnetic fields. The existence of a non-ferromagnetic component along with the ferromagnetic component is in agreement with the cluster model of another disordered cobaltite La$_{1-x}$Sr$_x$CoO$_3$, where a number of studies have shown the presence of non-ferromagnetic Co$_{3+}$ phases that coexist with ferromagnetic clusters [17, 20]. The ferromagnetic component can be extracted from the total magnetization by assuming that the total magnetization can be written as $M_{tot} = M_F + \chi_{AF}H$, where $M_F$ is the saturation value of the ferromagnetic component and $\chi_{AF}$ is the slope of the $M$ versus $H$ curve at high fields. Using this to fit the magnetization versus field curve above 12 T at 10 K, we estimate the saturation magnetization of the ferromagnetic component as $1.855(1)$ $\mu_B$/Co. The value of saturation magnetization of ferromagnetic clusters is smaller than that expected from the spin only value ($M_s = g\mu_B = 2.5$ $\mu_B$).
Figure 3. (a) Magnetization versus field at 10, 40, 180, 190, 200, 210, and 220 K. (b) Arrott plot ($M^2$ versus $H/M$) of the magnetization isotherms at 197, 199, 201, 202, 204, and 205 K. The solid black lines are straight line fits to the $M^2$ versus $H/M$ curve at high field, which are extrapolated to $H = 0$.

when both the Co$^{3+}$ ($S = 1$) and Co$^{4+}$ ($S = 3/2$) are in the IS state. It is to be noted that similar results for the difference in experimental and expected saturation magnetizations have also been reported for La$_{1-x}$Sr$_x$CoO$_3$ [17, 20]. On the basis of the band structure calculations, Ravindran et al [36] have shown that the hole doping in these materials reduces the ionicity, enhances the Co–O hybridization, and stabilizes the IS state. Due to enhanced Co–O hybridization the expected average Co moment is reduced compared to the prediction of a simple ionic model.

In figure 3(b), the $M–H$ isotherms around 200 K are plotted as $M^2$ versus $H/M$, which is known as the Arrott plot [37]. In these plots, the intercept of the linear fitting of high field data on the X and Y axis gives the inverse susceptibility and spontaneous magnetization respectively, and that passing through the origin gives the ferromagnetic transition temperature $T_C$. At 201 K, the value of spontaneous magnetization is 0.058 $\mu_B$/Co, which shows the presence of ferromagnetic interactions, and the line passing through origin will correspond to the $M^2$ versus $H/M$ curve lying in between 201 and 202 K indicating that the $T_C$ lies in between. The curves in the Arrott plot exhibit a downward curvature even at moderate fields. This suggests the possibility of non-mean-field-like behavior and therefore modified Arrott plots are better suited for more accurate determination of $T_C$. Above $T_C$, e.g. at 204 and 205 K, the spontaneous magnetization ($M_s$) is zero, indicating the absence of long range ferromagnetic ordering.

3.2. AC susceptibility

In order to get a better understanding of the magnetically ordered state, we have made ac susceptibility measurements at low fields which probe the dynamics of the system at the time scales decided by the measuring frequency range. The magnetization ($M$) of a system can be expressed in terms of the applied field ($H$) as

$$M(H) = M_0 + \chi_1 H + \chi_2 H^2 + \chi_3 H^3 + \cdots$$  

where $M_0$ is the spontaneous magnetization, $\chi_1$ is the linear susceptibility and $\chi_2, \chi_3, \ldots$ are the nonlinear susceptibilities, which can be identified with the Taylor series expansion of $M(H) = M_0 + (1/1!)(dM/dH)_{H=0}H + (1/2!)(d^2M/dH^2)_{H=0}H^2 + \cdots$.

3.2.1. Nature of magnetically ordered state. Figure 4 shows the real part of linear ac susceptibility ($\chi'_1$) measured in the ac field of 2.21 Oe and frequency 1131, 333, 131, 11, and 1 Hz. $\chi'_1$ exhibits a broad peak similar to that of ZFC magnetization and the peak position ($T_B$) in $\chi'_1$ increases on increasing the measuring frequency (\nu) (see the inset of figure 4), which is a common feature of spin-glass, cluster-glass, and superparamagnetic systems; and the presence of frequency dependence in $T_B$ clearly rules out the possibility of the normal long range ferromagnetic state. The frequency dependence in $\chi'_1$ is quantified as $\Phi = \ldots$
mainly consist of small antiferromagnetic clusters (average frequency \(\chi\)) superparamagnets or spin/cluster-glasses; on increasing the frequency \(\chi\), i.e. \(\chi\) are zero. \(\chi\) is observed in the presence of a superimposed external dc field or an internal field which originates from magnetically correlated spins. For canonical spin-glass the coefficient of even powers of \(H\) in equation (1) are zero. The real part of nonlinear susceptibility \(\chi^\prime\) is plotted in figure 5(a). \(\chi^\prime\) is zero in the paramagnetic phase, has a small positive peak at 202 K, then has a large negative peak around 167 K, and thereafter it slowly approaches zero. The strength of negative peaks in \(\chi^\prime\) diminishes on increasing the ac frequency. Below \(T_c\), the negative value of \(\chi^\prime\) clearly shows the presence of ferromagnetic ordering, which also rules out the presence of a canonical spin-glass state, but the possibility of coexistence of a spin-glass phase with ferromagnetic clusters remains open.

Figure 5(b) shows the temperature dependence of the real part of the third harmonic of the ac susceptibility (\(\chi^\prime\)) at different measurement frequencies. At the lower frequencies \(\chi^\prime\) exhibits a broad negative peak, similar to superparamagnets or spin/cluster-glasses; on increasing the frequency \(\chi^\prime\) changes sign, similar to ferromagnets \([43, 44]\), and on further increasing the frequency a positive peak in \(\chi^\prime\) is observed. In the critical regime, the characteristic relaxation time \((\tau)\) depends on the dynamic spin–spin correlation length \((\xi)\) as \(\tau \propto \xi^z\), where \(z\) is the dynamic critical exponent. On increasing the measurement frequency \((\nu)\), the time scale of relaxations that can be probed through ac susceptibility measurement decreases, and therefore the accessible region of relaxations in the ac susceptibility measurements shifts towards smaller \(\tau\) and \(\xi\). When accessible \(\xi\) reduces to the length scale of ferromagnetic clusters, then the contribution from within ferromagnetic clusters dominates \(\chi^\prime\) and we get a ferromagnetic-like critical behavior in \(\chi^\prime\). At 673 Hz and above, \(\chi^\prime\) exhibits a positive peak. The strength of this peak increases on (a) increasing the measurement frequency and (b) lowering the ac field (see inset of figure 5(b)). For antiferromagnets with coordination number \(n < 6\), in the framework of the Bethe approximation, \(\chi^\prime\) is always positive. It grows as temperature increases towards the Néel temperature \((T_N)\) and exhibits a discontinuity at \(T_N\) \([44]\). Experimentally, a positive peak in \(\chi^\prime\) has been observed in an antiferromagnet with \(n \leq 6\) \([45]\). This suggests that the observed positive peak in \(\chi^\prime\) at high ac frequencies is due to the presence of antiferromagnetic clusters. The average size of these antiferromagnetic clusters is expected to be smaller than that of ferromagnetic clusters. This is because, at higher ac frequencies, the contribution from regions of smaller relaxation time (and so smaller correlation length) determines the overall behavior of \(\chi^\prime\). On the basis of this, we infer that the non-ferromagnetic phases discussed in section 3.1.2 mainly consist of small antiferromagnetic clusters (average size smaller than that of ferromagnetic clusters) that coexist with a percolating backbone of ferromagnetic clusters.

3.2.2. Absence of spin- or cluster-glass-like transition. After discarding the possibility of a canonical spin-glass state on the basis of the nonzero value of \(\chi\), we need to identify the origin of the frequency dependence in \(T_B\) from the remaining possibilities, which are a cluster-glass, superparamagnetism, and the coexistence of a spin-glass phase with ferromagnetic clusters. In the first two cases, relaxing entities are superspins, i.e. the moment of a single magnetic domain (cluster), while for the last case the relaxing entities are the atomic spins. It is quite difficult to distinguish whether the slowing down in the spin dynamics is due to progressive thermal blocking or due to spin-glass-like cooperative freezing of the fluctuating entities. To determine the nature of spin dynamics, we have measured the third harmonic of ac susceptibility (\(\chi^\prime\)), which is proportional (and opposite in sign) to spin-glass susceptibility (\(\chi_{SG}\)). The negative divergence of \(\chi^\prime\) at \(T_B\) in the limit of \(H \to 0\) gives direct evidence of the spin-glass-like critical
slowing down of the fluctuating entities and hence can be used as an unambiguous test to probe the presence of spin- or cluster-glass phase [43, 46, 47]. The temperature dependence of the real part of the third harmonic of ac susceptibility at 131 Hz and at different ac fields is plotted in figure 6. The magnitude of the peak in $\chi_3 (\chi_3^{\prime}(\text{max}))$ does not diverge as $H \to 0$, which clearly shows that the fluctuating entities do not freeze in a spin- or cluster-glass state. We do not observe any ZFC memory effect, which further supports the absence of spin- or cluster-glass-like freezing in the system. These results suggest that the observed frequency dependence in $\chi_3$ is possibly due to progressive thermal blocking of fluctuating entities.

3.2.3. Superparamagnetic behavior of ferromagnetic clusters.

The existence of superparamagnetic behavior, i.e. progressive thermal blocking of single domain magnetic clusters, is further substantiated by Wohlfarth’s model of superparamagnets, which shows that the magnetization of an ensemble of magnetic clusters is given by [48, 49]

$$M = n\langle\mu\rangle L(\langle\mu\rangle H/k_B T) \quad (2)$$

where $n$ is the number of clusters per unit volume, $\langle\mu\rangle$ is the average magnetic moment of the clusters, $k_B$ is the Boltzmann constant, and $L(x)$ is the Langevin function. Above the blocking temperature ($T_B$), the expansion of the Langevin function in powers of $H$ gives

$$\chi_1 = n\langle\mu\rangle^2/3k_B T = P_1/T \quad (3)$$

and

$$\chi_3 = (n\langle\mu\rangle^3/45)k_B T^3 = P_3/T. \quad (4)$$

Equations (3) and (4) show that for superparamagnetic clusters, above $T_B$, $\chi_1$ and $\chi_3$ vary as linear functions of $T^{-1}$ and $T^{-3}$ respectively. Figure 7 shows $\chi_1$ versus $T^{-1}$ and its inset shows $\chi_3$ versus $T^{-3}$ above $T_B$. $\chi_1$ and $\chi_3$ curves show nonlinearity up to 185 K (above $T^{-1} \approx 5.41 \times 10^{-3}$ K$^{-1}$ and $T^{-3} \approx 1.58 \times 10^{-7}$ K$^{-3}$), and thereafter exhibit a linear behavior. The presence of curvature between $T_B$ and 185 K is possibly due to a large variation in the size of ferromagnetic clusters. In the linear region, the ratio of the fitting parameter $P_3$ and $P_1$ is used to estimate the average value of $\langle\mu\rangle$, which is around $1.83 \times 10^5 \mu_B$, where $\mu_B$ is the effective Bohr magneton. Such a large value of $\langle\mu\rangle$ is generally observed in superparamagnetic clusters. This is because the cluster consists of a large number of atomic spins each having a magnetic moment of a few $\mu_B$ (while normal paramagnets only have the atomic spins). Since $\langle\mu\rangle = M_S V$, where $M_S$ is the saturation magnetization and $V$ is the volume of cluster, assuming the clusters to be spherical, the average size of the clusters is around 15 nm. A large variation in the cluster size from the average value is expected. The average size of the magnetic clusters is much smaller than the crystallite size ($\approx 85$ nm calculated from x-ray diffraction), which indicates that each crystallite may contain a number of ferromagnetic clusters. Combining this with the results of low temperature isothermal magnetization of section 3.1.2 and the frequency dependence of the third harmonic of ac susceptibility of section 3.2.1, we infer that each crystallite of the system consists of percolating ferromagnetic clusters coexisting with smaller antiferromagnetic clusters.

3.2.4. Inter-cluster interaction. The ferromagnetic clusters coexisting with the non-ferromagnetic phases may interact with each other directly through dipole–dipole interaction or via the non-ferromagnetic matrix through exchange interactions [50]. The degree of inter-cluster interaction and its effect on fluctuation dynamics is studied by fitting the frequency dependence of $T_B$ with Néel–Arrhenius, Vogel–Fulcher, and scaling laws [51]. To perform these
fittings we need \( T_B \) and relaxation time (\( \tau \)) for different measurement frequencies; \( \tau = \omega^{-1} \) while \( T_B \) is obtained by the GaussAmp fitting of the corresponding peak in \( \chi' \) (see figure 4) in the temperature range of approximately 160–174 K. The results of these fittings are shown in figure 8. For an ensemble of non-interacting superparamagnets, the relaxation time \( \tau \) follows the Néel–Arrhenius law [51]

\[
\tau = \tau_0 \exp \left( \frac{E_a}{k_B T} \right)
\]

(5)

where \( E_a \) is the average anisotropy energy barrier, \( \tau_0 \) is the time constant corresponding to the characteristic attempt frequency, and \( k_B \) is the Boltzmann constant. The experimentally observed \( \tau_0 \) values for non-interacting superparamagnets are in the range of \( 10^{-8} - 10^{-13} \) s [52]. Inset (a) of figure 8 shows the fitting of equation (5) to \( \ln \tau \) versus \( T_B^{-1} \) data, which gives \( \tau_0 \approx 10^{-402} \) s and \( E_a = 13.31 \) eV. The fitting of the Néel–Arrhenius law yields unphysical values, which rule out the possibility of non-interacting dynamics and hint at the presence of cooperative dynamics due to inter-cluster interaction. The dynamics of interacting superparamagnets is described by the Vogel–Fulcher law [51]

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

(6)

where the temperature \( T_0 \), which has a value between zero and \( T_B \), is often related to the strength of inter-cluster interaction. The parameters \( \tau_0, \tau_0, \) and \( E_a/k_B \) are obtained by fitting equation (6) to \( \ln \tau \) versus \( T_B \), but this method of fitting suffers from unequal weightage given to some experimental data points. In order to fit equation (6) with nearly equal weight to all data points, we rewrite equation (6) as

\[
\ln \tau = \ln \tau_0 + \left( \frac{E_a}{k_B (T - T_0)} \right).
\]

(7)

Now taking the \( T_0 \) value obtained from fitting equation (6) to \( \ln \tau \) versus \( T_B \) data as a starting point, \( T_0 \) is varied in steps of 0.1 K and equation (7) is fitted to the data of figure 8. The best fit gives the correct value of \( T_0 \). We get \( T_0 = 164.3(1) \) K, \( \tau_0 = 1.1(6) \times 10^{-10} \) s, and \( E_a/k_B = 70(2) \) K. The \( \tau_0 \) value obtained from the Vogel–Fulcher fitting is orders of magnitude larger than the spin-flip time of atomic magnetic moments (\( \sim 10^{-13} \) s). This strongly supports the view that the fluctuating entities are spin clusters with a significant inter-cluster interaction among them. Strong inter-cluster interactions can give rise to spin-glass-like cooperative freezing, and in this case the frequency dependence of the peak in \( \chi'_1 \) is expected to follow the power law divergence of the standard critical slowing down given by dynamic scaling theory [29, 51]

\[
\tau = \tau_0 (T/T_g - 1)^{-\zeta \nu'}
\]

(8)

where \( \tau \) is the dynamical fluctuation time scale corresponding to the measurement frequency at the peak temperature of \( \chi'_1 \), \( \tau_0 \) is the spin flipping time of the relaxing entities, \( T_g \) is the cluster-glass (or spin-glass) transition temperature in the limit of zero frequency, \( \zeta \) is the dynamic scaling exponent, and

\( \nu' \) is the critical exponent. In the vicinity of the cluster-glass transition, the spin-cluster correlation length \( \xi \) diverges as \( \xi \propto (T/T_g - 1)^{-\nu'} \) and the dynamic scaling hypothesis relates \( \tau \) to \( \xi \) as \( \tau \sim \xi^{\nu} \). To fit the data with nearly equal weight, it is convenient to rewrite equation (8) as

\[
\ln \tau = \ln \tau_0 - \zeta \nu' \ln (T/T_g - 1).
\]

(9)

The inset (b) of figure 8 show \( \ln \tau \) versus \( \ln (T/T_g - 1) \). Starting with the \( T_g \) value obtained from fitting of equation (8) to \( \ln \tau \) versus \( T_B \) data, \( T_g \) is varied in steps of 0.1 K to obtain the best fit of equation (9) to the data of inset (b) of figure 8. This gives \( T_g = 165.9(1) \) K, \( \tau_0 \sim 10^{-21} \) s, and \( \zeta \nu' = 10.3(3) \). The value of exponent \( \zeta \nu' \) is somewhat higher than that observed in the case of spin-glasses (2–10) and \( \tau_0 \) is orders of magnitude smaller than the values reported for cluster-glasses (\( 10^{-6} - 10^{-10} \) s) and spin-glasses (\( 10^{-11} - 10^{-13} \) s). The value of \( T_0 \) is even smaller than the spin-flip time of a single atom (\( \sim 10^{-13} \) s), which is unphysical, and this indicates that the spin-cluster dynamics in the system does not exhibit critical slowing down on approaching \( T_g \) as expected from the dynamic scaling theory. Thus, it can be concluded that the inter-cluster interactions among the ferromagnetic clusters are significant, but not strong enough to cause a spin-glass-like transition.

3.3. Further discussion

The presence of significant inter-cluster interaction can also be reaffirmed from the field dependence of the peak temperature (\( T_B \)) in ZFC magnetization curves. For an Ising spin-glass, the spin-glass mean field theory predicts a critical de Almeida–Thouless (AT) line in \( H–T \) space which marks the spin-glass phase transition [53]. Above
the AT line the large field destroys the frozen spin state. The spin-glass transition temperature corresponds to the peak in ZFC magnetization \( T_p \) and the AT line predicts that \( T_p \propto H^{2/3} \). The AT-line-like field dependence of \( T_p \) is not unique to the spin- or cluster-glass transition but has also been observed in some interacting superparamagnets which otherwise undergo a progressive thermal blocking [33, 54]. In figure 9 we have plotted the field dependence of \( T_p \), which fits well with the AT line giving a zero field spin-glass transition temperature \( T_g \) of 172(1) K. Since our ac susceptibility measurements have ruled out the possibility of a spin- or cluster-glass-like freezing, the existence of the AT line in \( H-T \) space clearly indicates the presence of a significant inter-cluster interaction in the system. The inter-cluster interaction can originate from different types of magnetic interaction and the strength of these interactions generally depends on the packing density of ferromagnetic clusters. These magnetic interactions include the long range dipole–dipole interaction among the ferromagnetic clusters along with the possibilities of exchange, tunneling exchange and superexchange interactions [50].

The absence of spin-glass phase in \( \text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3 \) is in contrast with \( \text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3 \), where spin-glass phase coexists with the percolating ferromagnetic clusters [18, 21]. The doping at the A site of \( \text{LaCoO}_3 \) with 50% Ba or Sr gives same hole concentration, and therefore the observed discrepancy in the magnetically ordered state of \( \text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3 \) and \( \text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3 \) can be only due to the difference in local lattice distortions caused by the difference in ionic radii of \( \text{Ba}^{2+} \) and \( \text{Sr}^{2+} \). The elastic neutron scattering of the Sr and Ba doped \( \text{LaCoO}_3 \) indicate the existence of an incommensurate magnetic ordering with antiferromagnetic correlations along with the ferromagnetic clusters [55, 56]. While for \( \text{La}_{1-x}\text{Ba}_x\text{CoO}_3 \) the strength of the incommensurate state increases and becomes commensurate on increasing \( x \), for \( \text{La}_{1-x}\text{Sr}_x\text{CoO}_3 \) the incommensurate state strengthens but remains incommensurate on increasing \( x \) [56]. This is because the enhanced local randomness in \( \text{La}_{1-x}\text{Ba}_x\text{CoO}_3 \) due to larger ionic radii of \( \text{Ba}^{2+} \) favor the growth of antiferromagnetic ordered phases. The existence of a competing incommensurate antiferromagnetic ordering along with ferromagnetic clusters possibly gives the spin-glass phase in \( \text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3 \). In \( \text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3 \) both the ferromagnetic and antiferromagnetic ordering are commensurate, resulting in coexisting antiferromagnetic and ferromagnetic clusters. The absence of spin-glass phase in \( \text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3 \) suggests that the spin-glass phase in \( \text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3 \) is associated with the presence of incommensurate antiferromagnetic ordering in the non-ferromagnetic phases.

4. Conclusions

In conclusion, we have performed a comprehensive set of dc magnetization, linear and nonlinear ac susceptibility measurements to understand the magnetic state of the hole doped disordered cobaltite \( \text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3 \). The results of isothermal magnetization suggest that the magnetically ordered state of the system consists of percolating ferromagnetic clusters coexisting with the non-ferromagnetic phases. The percolating ferromagnetic clusters possibly start a magnetic ordering around 201.5(5) K. The frequency dependence of the third harmonic of ac susceptibility suggests that the non-ferromagnetic phases mainly consist of antiferromagnetic clusters whose sizes are smaller than those of ferromagnetic clusters.

Below \( T_C \) the system exhibits thermomagnetic irreversibility and frequency dependence in the peak of ac susceptibility, which suggest the presence of spin-glass, cluster-glass, or superparamagnetic phases. The absence of field divergence in the peak of the third harmonic of ac susceptibility and absence of ZFC memory rule out the existence of spin- or cluster-glass phase and suggest that the observed spin dynamics is possibly due to superparamagnet-like thermal blocking of ferromagnetic clusters. This is in sharp contrast to \( \text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3 \), where the spin-glass phase coexists with the ferromagnetic clusters. Our analysis suggests that the existence of the spin-glass phase is associated with the presence of incommensurate antiferromagnetic ordering in the non-ferromagnetic phases, which in turn is determined by the degree of local lattice distortion caused by the doping of divalent ion. The superparamagnetic behavior of ferromagnetic clusters in \( \text{La}_{0.5}\text{Ba}_{0.5}\text{CoO}_3 \) is further confirmed by Wohlfarth’s model of superparamagnetism. The analysis of frequency dependence in the peak of ac susceptibility by Néel–Arrhenius, Vogel–Fulcher, and scaling laws suggest the existence of significant inter-cluster interaction among the ferromagnetic clusters, which is further confirmed by the existence of an AT line in the \( H-T \) space.

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