Spin-glass-like dynamics of ferromagnetic clusters in La$_{0.75}$Ba$_{0.25}$CoO$_3$

Devendra Kumar

UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore-452001, India

E-mail: deveniit@gmail.com and deven@csr.res.in

Received 3 April 2014, revised 11 May 2014
Accepted for publication 15 May 2014
Published 17 June 2014

Abstract
We report a magnetization study of the compound La$_{0.75}$Ba$_{0.25}$CoO$_3$ where the Ba$^{2+}$ doping is just above the critical limit for percolation of ferromagnetic clusters. The field cooled and zero-field cooled (ZFC) magnetization exhibit thermomagnetic irreversibility and the ac susceptibility shows a frequency dependent peak at the ferromagnetic ordering temperature ($T_C = 203$ K) of the clusters. These features indicate the presence of a non-equilibrium state below $T_C$. For the non-equilibrium state, the dynamic scaling of the imaginary part of the ac susceptibility and the static scaling of the nonlinear susceptibility clearly establish a spin-glass-like cooperative freezing of ferromagnetic clusters at 200.9(2) K. The assertion of the occurrence of spin-glass-like freezing of ferromagnetic clusters is further substantiated by ZFC ageing and memory experiments. We also observe certain dynamical features which are not present in a typical spin glass, such as: the initial magnetization after ZFC ageing first increases and then decreases with the waiting time; and there is an imperfect recovery of relaxation in negative temperature cycling experiments. This imperfect recovery transforms to perfect recovery for concurrent field cycling. Our analysis suggests that these additional dynamical features have their origin in the inter-cluster exchange interaction and cluster size distribution. The inter-cluster exchange interaction above the magnetic percolation level gives a superferromagnetic state in some granular thin films, but our results show the absence of a typical superferromagnetic-like state in La$_{0.75}$Ba$_{0.25}$CoO$_3$.

Keywords: disordered cobaltites, spin glass, cluster glass, superferromagnetism

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

1. Introduction

Magnetically ordered materials exhibit interesting physical properties when the spin–spin correlation length is limited to the range of a few nanometers [1]. The size of the correlation length can be limited by limiting the physical size of the material, by forming few-nanometer-size single-domain nanoparticles. Ensembles of such nanoparticles are observed to exhibit intriguing dynamical features, such as superparamagnetic-like thermal blocking, spin-glass-like cooperative freezing, and ferromagnet-like correlation between nanoparticle moments in the so-called superferromagnetic state [2]. The nature of the physical state in the nanoparticle assembly is determined by the competition between the anisotropy energy, the dipole interaction, and the exchange interaction. For a dilutely packed nanoparticle system a superparamagnetic state is observed, but for a densely packed nanoparticle system with strong dipolar interactions, a spin-glass-like cooperative freezing is reported [2–4]. The presence of additional exchange interaction in a densely packed nanoparticle system with strong dipolar interactions can also result in a superferromagnetic state [2, 5–8].

The size of the correlation length can also be limited even without limiting the physical size of the system. In a number of materials, e.g. in the phase-separated manganites (La$_{0.75}$Nd$_{0.25}$)$_{0.7}$Ca$_{0.3}$MnO$_3$, La$_{0.7-x}$Y$_x$Ca$_{0.3}$MnO$_3$ (0 $\leq x \leq 0.15$) and cobaltite La$_{1-x}$Sr$_x$CoO$_3$ (0.18 $\leq x \leq 5.0$), this happens due to the formation of short range ferromagnetic clusters in the paramagnetic matrix at the ferromagnetic transition [9–11]. The ferromagnetic clusters in manganites...
are metallic and are associated with the temperature-driven first-order insulator–metal transition. These clusters appear at the transition temperature, grow in number and size on lowering the temperature, and finally may undergo a spin-glass-like freezing on further decreasing the temperature. The inter-cluster interaction increases on decreasing the temperature and attains its peak value at the freezing temperature [9, 10]. Above the magnetic percolation level for ferromagnetic clusters, there is a finite possibility of an exchange interaction between the neighboring clusters in addition to the long range dipolar interaction. This additional exchange interaction, present above the magnetic percolation level for Fe nanoparticles in FeAg granular thin films, causes a crossover from a spin-glass-like state to a superferromagnetic state [12].

The presence of short range ferromagnetic clusters in cobaltites with formula La1−xAxCoxO3 (where A is the divalent ion Ba2+ or Sr2+) has been observed in a number of reports [11, 13–20]. The density of ferromagnetic clusters increases on increasing the Ba2+ or Sr2+ doping, and above a critical doping (xc), the ferromagnetic clusters percolate. The percolation occurs at xc = 0.2 for Ba2+ and xc = 0.18 for Sr2+ [17–20]. The ferromagnetic clusters tend to retain their cluster nature and do not completely agglomerate to form a continuous phase even above the percolation level [11, 16, 19, 20]. Below xc, both the Ba2+ doped and Sr2+ doped systems exhibit a spin-glass-like cooperative freezing [17, 20]. Above xc, ac susceptibility measurements on La1−xSrxCoxO3 show some characteristics of cluster-glass dynamics while no such signature has been detected for La1−xBa2+2xCoO3 (x = 0.2 and 0.3) [11, 19–21]. Recently a detailed study on La0.75Ba0.25CoO3 has suggested the presence of interacting superparamagnetic-like dynamics in the ferromagnetic clusters [16]. This makes the region between xc and x = 0.5 for Ba2+ doping interesting, as at one end we have the spin-glass-like dynamics, while at the other end we have the interacting superparamagnetic-like dynamics with a surprising absence of dynamical features in between.

In this work we have performed a comprehensive investigation of the magnetically ordered state of La0.75Ba0.25CoO3 which lies just above the critical doping for percolation. The ferromagnetic clusters in La0.75Ba0.25CoO3 will experience a long range dipolar interaction as well as a short range nearest neighbor inter-cluster exchange interaction, and, therefore, are good candidate materials for studying the interplay of these competing interactions in. Our results show that ferromagnetic clusters in La0.75Ba0.25CoO3 undergo a spin-glass-like cooperative freezing. In contrast to the cases for La1−xSr2+2xCoO3 (0.18 ⩽ x ⩽ 5.0) and La0.75−xY0.25Ca0.3MnO3 (0 ⩽ x ⩽ 0.15), the cluster-glass transition in La0.75Ba0.25CoO3 nearly coincides with the ferromagnetic ordering and the inter-cluster interaction is found to be unaffected by temperature. We observe, concurrently with the spin-glass-like dynamics, the signature of an additional dynamical mechanism which has been attributed to the exchange interactions between the ferromagnetic clusters. Our analysis also shows that unlike the case for FeAg granular films, the percolation of ferromagnetic clusters in La0.75Ba0.25CoO3 does not establish a typical superferromagnetic-like state in the system.

2. Experimental details

Polycrystalline samples of La0.75Ba0.25CoO3 are prepared through the pyrophoric method as described in our earlier work [16]. High purity (99.99% ) La2O3, BaCoO3, and Co(NO3)2·6H2O in stoichiometric ratio are dissolved in dilute nitric acid, and triethanolamine (TEA) is added to the final solution, keeping the pH highly acidic. This solution is dried at 100 °C; it finally burns and yields black powder. The black powder is pelletized and heated at 1125 °C for 12 h in air. These samples are characterized by means of XRD diffraction on a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation. The magnetization measurements are performed using a 7 T SQUID MPMS-XL (Quantum Design) and a 14 T PPMS-VSM (Quantum Design). The residual field in the 7 T SQUID MPMS-XL is set below 0.05 Oe by using the flux gate and compensation coils for ultralow field attachment, before performing the zero-field and low field magnetization, ageing,
and memory experiments. The data used in the scaling analysis were corrected for the demagnetization factor.

The x-ray data were analyzed by the Rietveld refinement method using FULLPROF software [22] and the results show that the sample is of single phase and crystallizes in a rhombohedral structure with space group $R\overline{3}c$, which is in agreement with the previous report [23]. Figure 1 displays the room temperature x-ray diffraction pattern of La$_{1-x}$Ba$_{x}$CoO$_3$ along with its Rietveld fit profile. The goodness of fit $\chi^2$ is 1.26 and the lattice parameters of the unit cell are $a = 5.4549(2)$ and $c = 13.3194(2)$. The oxygen content is determined by thermogravimetric analysis, and is close to its stoichiometric value of 3.0.

3. Results and discussion

3.1. Thermomagnetic irreversibility

Figure 2 shows the magnetization versus temperature curves at the fields of 5 Oe, 100 Oe, 500 Oe, and 10 000 Oe in field cooled (FC) and zero-field cooled (ZFC) protocols. In the FC protocol the sample is cooled to 5 K in the presence of an applied field and the data recorded in the heating run without changing the field. In the ZFC protocol the sample is cooled to 5 K in zero field, then a field is applied, and the data recorded in the heating run. Both FC and ZFC magnetization curves exhibit a paramagnetic–ferromagnetic transition on cooling, and the transition temperature ($T_C$) is estimated to be around 203 K from the temperature derivative of the 500 Oe FC magnetization curve (see the inset of figure 2). On further cooling, the ZFC magnetization curve diverges from the corresponding FC curve at a temperature $T_{irr}$ and exhibits a peak at a temperature $T_p$, while the FC magnetization curve continues to grow, albeit at a slower rate. On increasing the applied magnetic field, the ZFC peak flattens, and $T_{irr}$ and $T_p$ shift to lower temperatures. The existence of thermomagnetic irreversibility is generally observed in spin glasses [24–26], cluster glasses [27, 28], superspin glasses [29, 30], superparamagnets [31], and anisotropic ferromagnets [32–37]. The appearance of ferromagnetic ordering [14] at $T_C$ negates the possibility of an atomic spin-glass state.

The ferromagnetic state in these systems consists of small percolating ferromagnetic metallic clusters and the absence of an exchange bias effect rules out the possibility of the existence of a spin-glass phase at the interfaces of ferromagnetic clusters [13–18, 20, 38]. This suggests that the observed thermomagnetic irreversibility may have its origin in the dynamics of ferromagnetic clusters.

3.2. Dynamic scaling and ac susceptibility

The results of the ac susceptibility measurements at 0.05 Hz, 0.1 Hz, 0.2 Hz, 0.4 Hz, 0.9 Hz, and 1.8 Hz at 3 Oe ac field are displayed in figure 3. The real part of the ac susceptibility ($\chi'$) exhibits a peak at the ferromagnetic transition, but, as shown in the inset of figure 3, in contrast to the case for long range ferromagnets, the peak temperature ($T_i$) increases on increasing the measurement frequency. The existence of a frequency dependence for the peak position of $\chi'$ indicates that the correlation length of the ferromagnetic order does not diverge at $T_C$. This frequency dependence for the peak of $\chi'$ is detectable only below 2 Hz. This is possibly due to strong contributions coming from within the ferromagnetic regions at higher frequencies. Sazonov et al [21] failed to detect the frequency dependence in $\chi'$, possibly due to higher measurement frequencies. Unlike the case for La$_{1-x}$Sr$_x$CoO$_3$ (0.18 $\leq x \leq 5.0$) [11, 19], no secondary peak or hump in $\chi'$ is observed. The frequency dependence in the peak of $\chi'$ is generally manifested in non-equilibrium magnetic states, such as spin glass, cluster glass, superspin glass, and superparamagnets, and the parameter $\Phi = \Delta T_i/(T_i \log(f))$ which quantifies this dependence is observed to be around 0.02–0.005 for spin glass, cluster glass, superspin glass, and interacting superparamagnets, and around 0.1–0.3 for non-interacting superparamagnets [39–43]. From the data shown in the inset of figure 3 we obtain $\Phi$ to be around 0.0005. Since the possibilities of an atomic spin-glass state and of a spin-glass phase at the interfaces of ferromagnetic clusters have already been ruled out, the observed frequency dependence could be present because of spin-glass-like freezing or superparamagnet-like thermal blocking of interacting ferromagnetic clusters.

If the observed frequency dependence of $T_i$ is due to critical slowing down of fluctuating clusters, as in the case of the spin-glass transition, the spin-cluster correlation length ($\xi$) should diverge as $\xi \propto e^{-\nu z}$ on approaching $T_i$ from $T > T_i$. Here $T_i$ is the cluster-glass transition temperature at the zero-field dc limit, $\nu = (T - T_g)/T_g$ is the reduced temperature, and $\nu$ is the static critical exponent. The relaxation time ($\tau$) is related to the correlation length ($\xi$) as $\tau \propto \xi^\nu$ where $z$ is the dynamic critical exponent. Thus for a cluster-glass transition, the relation for the relaxation time $\tau$ (corresponding to a given measurement frequency $f$) can be written as

$$\tau = \tau_0 (T/T_g - 1)^\nu,$$

where $\tau_0$ is the spin flipping time of fluctuating spin clusters. For a given measurement frequency $f$, the peak temperature of the corresponding $\chi'(f)$, i.e. $T_i$, is associated with the
cluster-glass transition temperature. The imaginary part of the ac susceptibility ($\chi''(f)$) also exhibits a frequency dependent peak, and, in this case, the inflection point in $\chi''(f)$ is identified as the cluster-glass transition temperature ($T_f$). Although $T_f$ calculated from $\chi'(f)$ and that calculated from $\chi''(f)$ are expected to show qualitatively similar features, the frequency dependence in $\chi''(f)$ is more pronounced, and therefore estimation of $T_f$ from the inflection point of $\chi''(f)$ is more accurate. For 0.05 Hz, the error in estimation of $T_f$ is large, and so it has been left out of the fitting process. Figure 4(a) shows the fitting of equation (1) to $\tau$ versus $T_f$ data following the procedure described in [16]. There is a good fit with the data with $\tau_0 \sim 10^{-38}$ s, $T_g = 200.9(1)$ K, and $z\nu = 18(1)$. While the good fitting of equation (1) to the data suggests the possibility of a spin-glass-like phase transition, the value of the fitting parameter $\tau_0$ is unphysical and $z\nu$ is outside the range for a canonical spin glass (4–10) [44, 45], but is close to the values reported for cluster glass and superspin glass (10–15) [29, 30, 46–48]. The anomaly in $\tau_0$ could be due to error in the estimation of the fitting parameter caused by the limited span of the frequency range.

In the critical slowing down description of the spin-glass phase transition, $\chi''(\omega, T)$ should behave according to the dynamic scaling equation proposed by Geschwind et al [49]:

$$T\chi''(\omega, T)e^{-\beta} = g(\omega e^{-z\nu}),$$

(2)

where $\omega = 2\pi f$, $\beta$ is the critical exponent corresponding to the order parameter, and $g$ is a universal function of its argument. If the frequency dependence in $\chi''$ is indeed due to a spin-glass-like phase transition, then $\chi''$ curves of different frequency should collapse onto a single universal curve ($g$) for the proper values of the critical exponents $\beta$, $z\nu$ and (the transition temperature) $T_g$. As shown in figure 4(b), a nearly perfect collapse of the data over two decades of frequency is obtained for $T_g = 209.9(2)$ K, $\beta = 0.22(1)$ and $z\nu = 18(2)$, which confirms the presence of a spin-glass-like phase transition in the system. The values of the parameters $z\nu$ and $T_g$ are in agreement with the values obtained from equation (1).

3.3. Static scaling of nonlinear susceptibility

The magnetization ($M$) at the uniform applied field $H$ can be expanded in terms of nonlinear susceptibilities as

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

(3)

where $M_0$ is the spontaneous magnetization, $\chi_1$ is the linear susceptibility, and $\chi_2, \chi_3, \ldots$ are nonlinear susceptibilities. For an atomic spin glass, $M_0$ and the coefficients of even powers of $H$, i.e. $\chi_2, \chi_4, \ldots$ are zero, while the coefficients of the odd powers of $H$, i.e. $\chi_3, \chi_5, \ldots$ diverge as $T$ approaches $T_g$ in the critical regime [50–52]. For cluster glass, if the nonlinear response of isolated ferromagnetic clusters is small, the coefficients of the odd powers of $H$ will also diverge in the critical regime, like for the case for atomic spin glass [53]. The overall nonlinear susceptibility $\chi_{nl}$ which diverges in the critical temperature regime in a spin-glass system can be written as

$$\chi_{nl} = \chi_1 - M/H = \chi_2 H^2 + \chi_3 H^3 + \ldots$$

(4)
The phenomenological theory for spin glass given by Suzuki predicts that $\chi_{nl}$ should follow the static scaling relation [50]

$$\frac{\chi}{H^2} = \frac{\beta}{\gamma} + F(H)$$

or

$$\chi_{nl} = H^{\beta/(\beta+\gamma)} G(H^{\beta/\gamma})$$

where $\epsilon = (T - T_g)/T_g$ is the reduced temperature, $\beta$ is the critical exponent for the spin-glass order parameter, $\gamma$ is the critical exponent for the spin-glass susceptibility, and $F(x)$ and $G(x)$ are the scaling functions. The scaling is achieved by plotting $\chi_{nl}/H^{2(\beta/\gamma)}$ versus $H^{2/\gamma}$ for $\chi_{nl}$ at different fields and varying the parameters $T_g$, $\beta$, and $\gamma$ such that all data collapse onto a master curve. In the limit of $\epsilon \to 0$ the abscissa and ordinate have spans of many decades, and, therefore, are plotted on log scales. The log scale plotting gives equal weightings to all data points irrespective of their accuracy, which sometimes hides a departure from good scaling [24, 54]. To test the scaling equation in a better way, Geschwind et al [54] have rewritten the scaling equation such that the argument of the scaling function is linear in $\epsilon$:

$$\chi_{nl} = H^{\beta/(\beta+\gamma)} G(\epsilon/H^{\beta+\gamma})$$

The contribution of nonlinear susceptibilities to the magnetization diminishes as $H$ approaches zero, and in this limit, the magnetization above $T_g$ gives a reasonable approximation of $\chi_1$. We have used the magnetization at 0.5 Oe as the approximate value of $\chi_1$. Figure 5 shows the scaling plot obtained using equation (6) for the data at 10 Oe, 50 Oe, 200 Oe, and 1000 Oe. The data taken at four different fields collapse best onto a master curve for $\beta = 0.22$, $\gamma = 40$, and $T_g = 200.9$ K. The reasonable scaling of $\chi_{nl}$ from equation (6) supports the occurrence of a spin-glass-like phase transition at $T_g$. The values of the parameter $\beta$ and $T_g$ are in agreement with those for the dynamic scaling. The parameter $\beta$ lies in the range for cluster glass or superspin glass, while the parameter $\gamma$ is large in comparison to typical values observed for spin glass, cluster glass, or superspin glass [9, 45, 53, 55].

### 3.4. Ageing and memory experiments

The existence of a spin-glass-like phase transition in La$_{0.75}$Ba$_{0.25}$CoO$_3$ is also investigated through ageing and memory experiments. In FC (ZFC) ageing experiments, the system is cooled from 250 K to the temperature of ageing ($T_a$) in the presence of a field $H_a$ (zero field), and at $T_a$, after an isothermal waiting time of $t_w$ s, the field is switched off (field $H_a$ is applied) and the magnetization is recorded as a function of time. The results of field cooled ageing experiments at 80 K and 50 K for $H_a = 500$ Oe are presented in figure 6(a) and its inset, respectively. The decay of the thermoremanent magnetization exhibits the effect of the waiting time dependence which has been reported to occur in superparamagnets with a distribution of anisotropy energy barriers, as well as in systems with a spin-glass-like transition [4]. The value of the initial magnetization observed after switching off the field at 80 K increases on increasing the waiting time, like...
that for superparamagnets or spin glass, but exhibits a complex behavior at 50 K. The ageing experiments performed in the ZFC protocol show distinct behavior for superparamagnet and spin-glass systems. For superparamagnets, the waiting time dependence in ZFC ageing is either absent or significantly small (when several competing sources of anisotropy are present) in comparison to the waiting time dependence of FC ageing, while for spin-glass systems, a strong waiting time dependence is observed for both FC and ZFC ageing [4, 26]. Figure 6(b) shows the results of ZFC ageing experiments at $T = 50$ K and $H_0 = 100$ Oe. The presence of a strong waiting time dependence in ZFC ageing, as in the case of FC ageing, reconfirms the presence of a spin-glass-like transition in the system. The observed time dependence in the magnetization is fitted with a stretched exponential decay:

$$M(t) = M_0 - M_g \exp\left(-\frac{t}{\tau^{\beta}}\right),$$

(7)

where $M_0$ is the contribution of the intrinsic ferromagnetic component, $M_g$ is the initial magnetization of the glass component, $\tau$ is the time constant, and $\beta$ represents the distribution of energy barriers with $0 \leq \beta \leq 1$ for spin glass. Equation (7) fits well to the time dependent magnetization data of figure 6(b) and the fitting parameters are shown in table 1. The parameters $M_g$ and $\tau$ increase while $\beta$ decreases on increasing the waiting time. In spin-glass systems, the magnetization at $t = 0$, i.e. $M(0)$, is observed to decrease on increasing the waiting time ($t_w$) [4, 26, 56], but in La$_{0.75}$Ba$_{0.25}$CoO$_3$, it first increases and then decreases. The ZFC ageing experiments performed at 10 K (not shown here) also give similar results. A comparison of the waiting time dependence of $M(0)$ at 50 K and 10 K is shown in the inset of figure 6(b). A similar behavior of $M(0)$ is also observed in the ZFC ageing of ferromagnetic La$_{0.3}$Ca$_{0.7}$MnO$_3$ (18 nm) and antiferromagnetic La$_{0.2}$Ca$_{0.8}$MnO$_3$ (15 nm) nanoparticles [57, 58]. The initial increase in $M(0)$ with $t_w$ suggests the presence of an additional dynamical mechanism along with spin-glass-like freezing. For La$_{0.3}$Ca$_{0.7}$MnO$_3$ nanoparticles, the additional dynamic features have been claimed to be arising from the development of a superferromagnetic (SFM)-like state, i.e. the development of ferromagnetic-like correlation among the super spins [57].

For spin glass, Lundgren et al. have suggested that for ZFC ageing the quantity $S(t) = (1/H)(dM(t)/dt)$ is proportional to the spectral density of relaxation times ($g(\tau)$), and therefore, $S(t)$ versus $t$ plots give an estimate of $g_{\text{sw}}(t = \tau)$ for given $t_w$. As $t_w$ increases, $g_{\text{sw}}(\tau)$ shifts towards longer relaxation times and peaks around $t_w$ [56, 59, 60]. Figure 6(c) shows the $S(t)$ versus $\ln t$ curves for various values of $t_w$. As expected for a spin-glass system, we get a peak in $S(t)$ at $t_{\text{sw}}$, which shifts to higher $t$ on increasing $t_w$, but the order of the shift is relatively small in comparison to that for atomic spin glass. For atomic spin glass, $t_{\text{sw}} \approx t_w$, while in our case, $t_{\text{sw}} > t_w$ and shows a weak $t_w$ dependence. $t_{\text{sw}}$ varies from 4760 s to 6144 s on changing $t_w$ from 600 s to 5000 s. The observed $t_w$ dependence of $t_{\text{sw}}$ resembles that reported for La$_{0.7-x}$Y$_{x}$Ca$_{0.3}$MnO$_3$ ($0 \leq x \leq 0.15$) manganites which exhibit a cluster-glass behavior and La$_{0.8}$Ca$_{0.2}$MnO$_3$ (18 nm) nanoparticles which exhibit a superspin-glass-like behavior [10, 57].

The results of ZFC memory experiments are displayed in figure 6(d). In a ZFC memory experiment, the system is cooled in zero field from 300 K to 10 K with an intermediate stop of $10^3$ s at 130 K, and at 10 K, a 100 Oe field is applied and the magnetization $(M_{\text{ZFC ref}})$ is recorded in the heating run. The reference ZFC magnetization $(M_{\text{ref}})$ is also recorded under the same protocol but without an intermediate stop. The difference in magnetization, i.e. $\Delta M = M_{\text{ZFC ref}} - M_{\text{ZFC}}$, versus temperature exhibits a broad dip at around 140 K which signals that the system remembers its ageing at the intermediate stop during the cooling run. The memory in the ZFC protocol is only observed in systems undergoing a spin-glass-like cooperative freezing, and therefore, the observation of ZFC memory in figure 6(d) confirms the existence of a spin-glass-like state in La$_{0.7-x}$Ba$_{0.25}$CoO$_3$ [4, 26, 61, 62]. Here we note that in contrast to the case for atomic spin glass, the observed dip in ZFC memory is broad and does not exhibit a complete rejuvenation. Such a behavior is generally observed in superspin glass or cluster glass where the microscopic flipping time of the fluctuating magnetic entities (superspins) is much longer than that for atomic spin glass, and therefore, the observation time in units of the microscopic flipping time is relatively short in comparison to that for atomic spin glass [57, 58, 63, 64]. Because of this, the length scales probed during the experimental time scale are shorter, and the condition for rejuvenation, i.e. the length scales probed during the experimental time scale being larger than the so-called overlap length, is not satisfied [63]. The absence of complete rejuvenation in the ZFC memory may also occur if the probing field is strong enough to perturb the intrinsic non-equilibrium dynamics of the spin-glass system.

### 3.5. Temperature-field cycling and relaxation

The relaxation experiments discussed in the previous section are complemented with an intermediate negative thermal cycling with and without field change. Figure 7(a) shows the result of temperature cycling without field change. Figure 7(b) shows the relaxation time dependence at 50 K and 10 K. According to Sun et al., for superspin glass and cluster glass the relaxation for time $t_1$ should be a continuation of the relaxation at $t_1$ [26, 61, 65]. The inset of figure 7(a) shows the relaxation at $t_1$ and $t_5$. The relaxation data of figure 6(b).

### Table 1. Fit parameters obtained from the fitting of equation (7) to the magnetization data of figure 6(b).

| $t_w$ (s) | $M_0$ | $M_g$ | $\tau \times 10^3$ | $\beta$ | $\chi^2$/DOF | $R^2$ |
|----------|-------|-------|-------------------|--------|-------------|-------|
| 0        | 0.0142 | 0.99920 | 57.30(8) 7.0(1) | 4.3(2) | 0.052(8) 0.00142 | 0.99920 |
| 6 x 10$^2$ | 74.77(9) 7.2(1) | 4.8(2) | 0.488(8) 0.00139 | 0.99921 |
| 2 x 10$^3$ | 61.26(9) 7.3(1) | 5.2(2) | 0.488(7) 0.00103 | 0.99941 |
| 5 x 10$^3$ | 54.5(1) 7.4(1) | 6.1(3) | 0.476(7) 0.00027 | 0.99982 |

$H_M(t) = 1/(t + 1/t^{\beta})$,
for \( t_3 \) has the same functional form as that for \( t_1 \) but is shifted upward. Figure 7(b) exhibits the relaxation under a similar protocol but with zero field between \( t_1 \) and \( t_3 \). As is clear from the inset of figure 7(b), the relaxation at \( t_3 \) is the continuation of that at \( t_1 \) without any apparent shift in magnetization as expected from a typical superspin glass or cluster glass. This indicates that a concurrent field cycling destroys the mechanism responsible for the observed additional upward shift in magnetization during the negative thermal cycling. The results of a similar set of negative thermal cycling experiments performed with and without field cycling under the FC protocol are shown in figures 7(c) and (d) respectively. The insets show the relaxation for \( t_1 \) and \( t_3 \). When the field remains zero during the temperature cycling, the relaxation at \( t_3 \) has the same functional form as that at \( t_1 \), but starts with a lower initial value. A concurrent field cycling along with temperature cycling (0 Oe, 50 K, \( t_1 \) s, -100 Oe, 40 K, \( t_2 \) s, -0 Oe, 50 K, \( t_3 \) s) nearly removes this shift, and, in this case, relaxation for \( t_3 \) is a continuation of relaxation for \( t_1 \), like the cases observed for superspin glass and cluster glass. The results of negative temperature cycling without the field change in the ZFC and FC protocols support the finding of ZFC ageing experiments (discussed in section 3.4) that there exists an additional relaxation mechanism besides the usual cluster-glass relaxation. This additional relaxation mechanism seems to enhance the effect of the cluster-glass relaxation, i.e. it contributes positively to the magnetization when spin clusters align during the relaxation process (ZFC ageing) but contributes negatively to the magnetization when spin clusters randomize during the relaxation (FC ageing). The field cycling probably blocks the continuous contribution of this additional relaxation mechanism to the magnetization during negative temperature cycling, and thus leaves us with a normal cluster-glass-like relaxation behavior.

4. Further discussion

The experimental results discussed in the previous sections clearly establish the existence of a spin-glass-like phase transition along with an additional concurrent dynamics in the so-called ferromagnetic cluster state of \( \text{La}_{0.75}\text{Ba}_{0.25}\text{CoO}_{3} \). The spin-glass-like behavior may arise due to cooperative freezing of ferromagnetic clusters or it can be due to the coexistence of a spin-glass phase with the ferromagnetic clusters. The absence of an exchange bias effect suggests the lack of a ferromagnetic spin-glass interface. This, along with the values of the critical exponents \( \nu \) and \( \beta \), the waiting time dependence of \( S(t) \), and the lack of complete rejuvenation in the ZFC memory, indicates that the spin-glass-like behavior is arising from the cooperative freezing of ferromagnetic clusters rather than atomic spins.

The existence of spin-glass-like dynamics in an assembly of ferromagnetic clusters requires (a) dense packing of the ferromagnetic clusters with random orientation of the anisotropy axes and (b) strong inter-cluster dipolar interactions. In \( \text{La}_{0.75}\text{Ba}_{0.25}\text{CoO}_{3} \), the ferromagnetic clusters with randomly oriented anisotropy axes percolate [13–15, 17, 18], and so there is also a reasonable possibility of exchange interaction between the neighboring ferromagnetic clusters. The exchange interaction between the ferromagnetic clusters could...
Figure 8. Relaxation rate versus time on a log scale at 175 K, 150 K, and 125 K. The straight lines show the fitting of equation (8) to the respective data.

Occur because of exchange bridges between the surface atoms of neighboring ferromagnetic clusters or could be due to tunneling exchange coupling between the neighboring metallic ferromagnetic clusters [5, 6, 66, 67]. The competing dipolar and inter-cluster exchange interactions in a disordered random anisotropy system can lead to a superferromagnetic state [2, 7, 12, 66, 68]. The superferromagnetic state exhibits dynamic features as in the cluster glass (or superspin glass); but in contrast to the cluster glass, which has a zero-thermoremanent magnetization in the limit of $n \to \infty$, the superferromagnet has a finite remanence [69–71].

The decay of the relaxation rate ($W(t)$) of the thermoremanent magnetization ($m(t)$) can be used to distinguish the cluster-glass (or superspin-glass) dynamics from that of the superferromagnet. According to the Monte Carlo simulations of Ulrich et al., $W(t)$ for an assembly of nanoparticles with dipole interaction decays as a universal power law after some crossover time $t_0$ [3]:

$$W(t) = \frac{d}{dt} \ln m(t) = At^{-n},$$  

(8)

where the exponent $n$ depends on the packing density of the nanoparticles and $A$ is a temperature dependent constant. Depending on the value of the exponent $n$, $m(t)$ decays as a stretched exponential $m(t) = m_0 \exp(-t/t_0^{1/\alpha})$ (for $n < 1$), a power law $m(t) = m_1 t^{-\alpha}$ (for $n = 1$), or a power law with finite remanence $m(t) = m_0 + m_1 t^{-\alpha}$ (for $n > 1$). The decay with exponent $n < 1$ is associated with dilute systems, $n = 1$ is associated with cluster glass or superspin glass, and $n > 1$ is associated with superferromagnets [3, 70, 71]. These theoretical predictions have been substantiated by relaxation measurements on granular multilayers, magnetic clusters, and nanoparticle assemblies [9, 70–76]. Experimentally, $n = 1$ ($n > 1$) is observed for cluster glass or superspin glass, while $n > 1$ is seen for superferromagnets. Mao et al have performed mean field calculations including both the dipolar and the exchange interactions among the nanoparticles, and their results show that $n = 1$ (with superspin-glass behavior) for small exchange interactions, which smoothly transforms to $n > 1$ (with superferromagnetic behavior) on gradually enhancing the strength of the exchange interaction keeping the dipolar interaction intact [8].

Figure 8 shows $W(t)$ versus time on a log–log scale at 175 K, 150 K, and 125 K. Here the system is cooled from 300 K to the respective relaxation temperatures under a field of 100 Oe, and after temperature stabilization, the field is switched off and the thermoremanent magnetization is recorded as a function of time. The fitting of equation (8) to the $W(t)$ versus time data gives $n = 0.99(7)$ at 175 K, $n = 0.89(4)$ at 150 K and $n = 0.93(3)$ at 125 K. The $n$ values are close to 1 (from the lower side), supporting a cluster-glass dynamics. We have also fitted the time dependence of the thermoremanent magnetization with a stretched exponential, a power law, and a power law with finite remanence, and only the power law function fits with reasonable parameters and error values. The power law with finite remanence fit gives a huge error in the fitting parameters. This, along with $n < 1$, rules out the possibility of superferromagnet-like dynamics and suggests that inter-cluster exchange interactions in La$_{0.75}$Ba$_{0.25}$CoO$_3$, if present, are relatively weak in comparison to the dipolar interaction. We also note that the value of the exponent $n$ remains nearly constant on changing the relaxation temperature from 125 K (0.6255 $T_g$) to 175 K (0.875 $T_g$) which indicates that the inter-cluster interaction remains nearly constant on approaching $T_g$. This behavior is quite different to those for other phase-separated manganites and cobaltites, for which $n$ increases on approaching $T_g$ due to the increase in inter-cluster dipolar interactions which has been attributed to enhancement in the cluster density [9, 73].

The presence of additional dynamic features in the cluster-glass state can be understood by taking into account the competition between the dipolar and exchange interactions. The energy $E_i$ of a cluster $i$ in an ensemble of ferromagnetic clusters can be written as

$$E_i = -KV(\hat{n}_i \cdot \hat{n}_i) + \sum_j (\mu_i \cdot \mu_j - 3(\mu_i \cdot \hat{r}_{ij})(\mu_j \cdot \hat{r}_{ij})) \frac{1}{r_{ij}^3}$$  

$$- \sum_j J_{ij} \mu_i \cdot \mu_j - \mu_i \cdot H,$$  

(9)

where $K$ is the anisotropy constant, $\hat{n}_i$ is the unit vector along the easy axis, $V_i$ is the volume, $\mu_i$ is the moment of the $i$th cluster, $r_{ij}$ is the distance between the $i$th and $j$th clusters, and $H$ is the applied field. $J_{ij}$ represents the exchange coupling between the nearest neighbors $i$ and $j$. The anisotropy energy favors the alignment of cluster moments along the easy axis $\hat{n}_i$, which may vary randomly from cluster to cluster. The first term of the dipolar energy favors antiferromagnetic coupling, while the second term attempts to align these clusters randomly. The anisotropy energy and the dipolar interaction in a densely packed cluster system give a spin-glass-like cooperative dynamics [3, 8]. The exchange energy favors the alignment of nearest neighbors, while the Zeeman energy favors the alignment of all the cluster moments along the field direction. The anisotropy energy gives two equal energy minima—one along and the other opposite to $\hat{n}_i$. The dipolar energy, the exchange energy, and the Zeeman energy may lower the energy of one of these minima and the cluster moment will transform to the low energy state by thermal activation. For weak exchange interaction and small field, the dominant anisotropy and dipolar energy
terms cause a cluster-glass-like dynamics [8]. The ensemble of ferromagnetic clusters in our system will have a cluster size distribution. The small clusters have a larger surface to volume ratio, and therefore, the exchange interaction may be more significant for small clusters embedded between the larger clusters. The dynamics of these small clusters will strongly depend on the alignment of their neighboring moments. The additional dynamical behavior observed in the ageing and negative temperature cycling experiments can possibly be understood on the basis of the above picture as follows:

(a) After a zero-field quench from above $T_g$, during zero-field ageing, the small embedded clusters will try to align according to their big neighbors because of the significant exchange interaction, while the big ones will relax according to the spin-glass model. The initial enhancement in magnetization is possibly a result of thermally activated alignment of small clusters, which is slowly overcome by the dominant spin-glass-like relaxation of larger clusters.

(b) The applied field lowers the energy of the easy axis direction pointing along the field. If this now becomes the low energy state, the activated alignment of cluster moments along the field direction will enhance the magnetization with time. Switching the field off favors the restoring of spin-glass-like ordering due to the prevalent dipole interaction. This causes the magnetization to decay with time. Because of the hierarchical nature of the dynamics of spin glass, the set of energy barriers relaxed at temperature $T$ are different from the set relaxed at $T - \Delta T$. When the temperature is lowered to $T - \Delta T$ after a relaxation at $T$, the contribution to the relaxation at $T - \Delta T$ comes from (i) the spin-glass-like relaxation of active clusters at $T - \Delta T$ and the exchange-induced activated alignment of their small neighbors and (ii) the exchange-induced activated alignment of small clusters by the frozen neighbors which were active at $T$.

(c) If the field is not changed during thermal cycling, then the exchange-induced thermally activated alignments of small clusters in the above processes (i) and (ii) add up. This gives an additional upward shift (downward shift) in magnetization for the ZFC protocol (for the FC protocol) when the temperature is brought back to $T$. Switching the field off (on) during relaxation in the ZFC protocol (the FC protocol) at $T - \Delta T$ weakens (ii), because now the Zeeman energy does not support (oppose) the alignment effort of the exchange energy. Additionally, the contribution from the alignment of small clusters in (i) will be opposite to that for (ii). Because of the opposite signs in the contributions from (i) and (ii), they tend to cancel each other, and therefore there is no significant shift in magnetization when the temperature is raised back to $T$.

5. Conclusions

We have performed a detailed investigation of La$_{0.75}$Ba$_{0.25}$CoO$_3$ which lies just above the critical doping for percolation of ferromagnetic clusters. Our results show an irreversibility in the FC–ZFC magnetization, and a frequency dependent peak in the ac susceptibility which coincides with the ferromagnetic ordering ($T_C = 203$ K) of the clusters. The contribution from the magnetic ordering within the clusters masks the frequency dependence of the ac susceptibility above 2 Hz. The FC–ZFC irreversibility and the frequency dependence for the peak of the ac susceptibility indicate the existence of a non-equilibrium state below $T_C$. The dynamic scaling of the imaginary part of the ac susceptibility, the static scaling of the non-linear susceptibility, and the ZFC ageing and memory experiments give conclusive evidence of spin-glass-like cooperative freezing of ferromagnetic clusters ($T_g = 200.9(2)$ K) in the non-equilibrium state.

The results of experiments on ZFC ageing in the non-equilibrium state indicate the existence of an additional dynamical mechanism besides the typical spin-glass dynamics. The presence of this additional dynamical mechanism is further substantiated by the relaxation under negative temperature cycling. Our analysis shows that this additional dynamical mechanism may possibly have its origin in the inter-cluster exchange interaction and cluster size distribution. The inter-cluster exchange interactions can create a superferromagnetic state in an ensemble of densely packed ferromagnetic clusters. The decay of the relaxation rate of the thermoremanent magnetization and the decay of the thermoremanent magnetization suggest the absence of a typical superferromagnetic state in La$_{0.75}$Ba$_{0.25}$CoO$_3$.

Acknowledgments

We are grateful to A Banerjee for support and discussions. We also acknowledge M Gupta for the XRD measurements.

References

[1] Batlle X and Labarta A 2002 J. Phys. D: Appl. Phys. 35 R15
[2] Bedanta S and Kleemann W 2009 J. Phys. D: Appl. Phys. 42 013001
[3] Ulrich M, García-Otero J, Rivas J and Bunde A 2003 Phys. Rev. B 67 024416
[4] Sasaki M, Jönsson P E, Takeyama H and Mamiya H 2005 Phys. Rev. B 71 104405
[5] Frandsen C, Ostenfeld C W, Xu M, Jacobsen C S, Keller L, Lefmann K and Mørup S 2004 Phys. Rev. B 70 134416
[6] Frandsen C and Mørup S 2005 Phys. Rev. Lett. 94 027202
[7] Bedanta S, Eimüller T, Kleemann W, Rhensius J, Stromberg F, Amaladass E, Cardoso S and Freitas P P 2007 Phys. Rev. Lett. 98 176601
[8] Mao Z and Chen X 2011 J. Phys.: Condens. Matter 23 226005
[9] Rivadulla F, Lo M A and Rivas J 2004 Phys. Rev. Lett. 93 167206
[10] Freitas R S, Ghivelder L, Damay F, Dias F and Cohen L F 2001 Phys. Rev. B 64 144404
[11] Nam D N H, Jonason K, Nordblad P, Khiem N V and Phuc N X 1999 Phys. Rev. B 59 4189
[12] Alonso Fdez M L, Barandiar J M, Svalov A, Fernández Barquin L, AlbaVenero D and Orue I 2010 Phys. Rev. B 82 054406
[13] Phelan D et al 2006 Phys. Rev. Lett. 96 027201
[14] Tong P, Yu J, Huang Q, Yamada K and Louca D 2011 Phys. Rev. Lett. 106 156407
