Journal of Alloys and Compounds 509 (2011) 4950–4953

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Spin-glass behavior and exchange bias in phase-separated $Nd_{0.85}Sr_{0.15}CoO_3$

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ARTICLE INFO

Article history:
Received 12 October 2010
Received in revised form 12 January 2011
Accepted 15 January 2011
Available online 22 January 2011

Keywords:
Spin glasses
Cobaltite
Exchange and superexchange
Exchange bias

ABSTRACT

The magnetic properties of $Nd_{0.85}Sr_{0.15}CoO_3$ have been systematically investigated by dc magnetization, ac susceptibility and magnetic relaxation. The dynamics scaling analysis of ac susceptibility and magnetic relaxation give sufficient evidence of the existence of a spin-glass phase, which can be ascribed to the complicated interactions among Co^{3+} and Co^{4+} ions in this phase-separated compound. The field-cooled magnetic hysteresis loop displays both horizontal and vertical shifts, i.e., the exchange bias effect, while no shifts are present with increase of the measuring field up to ±50 kOe. The results further sustain the picture of the spin-glass phase coexisting with other magnetic regions in the sample.

1. Introduction

The spontaneously phase-separated state in perovskite oxides has attracted much attention due to the importance of understanding the unique physical properties of these compounds, e.g., high temperature superconductivity in cuprates, colossal magnetoresistance effect and glassy behavior in manganites [1–4]. In the past few decades, there have been plenty of reports on the hole-doped cobaltites with perovskite structure, $Ln_{1-x}A_xCoO_3$ (Ln = rare earth element, A = alkli earth metal element), for peculiar electromagnetic properties [5–8]. As is well known, the Co^{3+} and Co^{4+} ions can exhibit several possible spin states for low-spin, intermediate-spin, and high-spin electronic configurations. The delicate interplay among lattice, charge, orbital and spin degrees of freedom induces the intriguing ground states in these systems, which display varieties of spontaneous phase-separation, and then intrigues unusual glassy behavior. Recently, an interesting phase diagram has been proposed for $La_{1-x}Sr_xCoO_3$ (LSCO) depending on the doping of Sr content [9–12]. The parent compound $LaCoO_3$ is a nonmagnetic insulator. The substitution of Sr^{2+} for La^{3+} in LSCO has some interesting effects: on the one hand, an equivalent number of Co^{3+} is converted into Co^{4+} ions to maintain the charge neutrality; on the other hand, the crystal-field changes and generally stabilizes the intermediate-spin state of Co^{3+} rather than the low-spin state [13]. Therefore, the competition between ferromagnetic (FM) double exchange interaction (Co^{3+}–Co^{4+}) and antiferromagnetic (AFM) superexchange interaction (Co^{3+}–Co^{3+}, Co^{4+}–Co^{4+}) results in different kinds of magnetic ordering with the change of doping concentration. For low doping range ($0 < x < 0.18$) spin-glass (SG) or cluster-glass (CG) state has been proposed. While with further increase in hole doping the short range FM clusters coalesce to attain long range magnetic ordering above a percolation threshold ($x > 0.18$).

With a view to understand the global phase behavior of hole-doped cobaltites, the electromagnetic properties of $Nd_{1-x}Sr_xCoO_3$ (NSCO) have been investigated in detail [14–16]. Similar to that reported in LSCO, the system of NSCO also exhibits analogous phase-separation scenario and phase diagram [14]. It is worth noting that Krimmel et al. observed the ferrimagnetic structure in $Nd_{0.67}Sr_{0.33}CoO_3$ induced by the antiparallel alignment of the two FM sublattices between Nd and Co by neutron powder diffraction [15]. In contrast to the LSCO at the same level of Sr doping, there is weak superexchange coupling between Nd and Co sublattices at low temperature, so the competition between FM and AFM interactions among Nd^{3+}, Co^{3+} and Co^{4+} ions may intrigue interesting glassy behaviors in NSCO. Meanwhile, the question whether there exists a classical SG phase or not below the percolation threshold $x = 0.18$ in the system of NSCO, still remains open. Therefore, it is necessary to explore the magnetic behavior in the intrinsically phase-separated NSCO. It is known that most of the unusual

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doi:10.1016/j.jallcom.2011.01.105

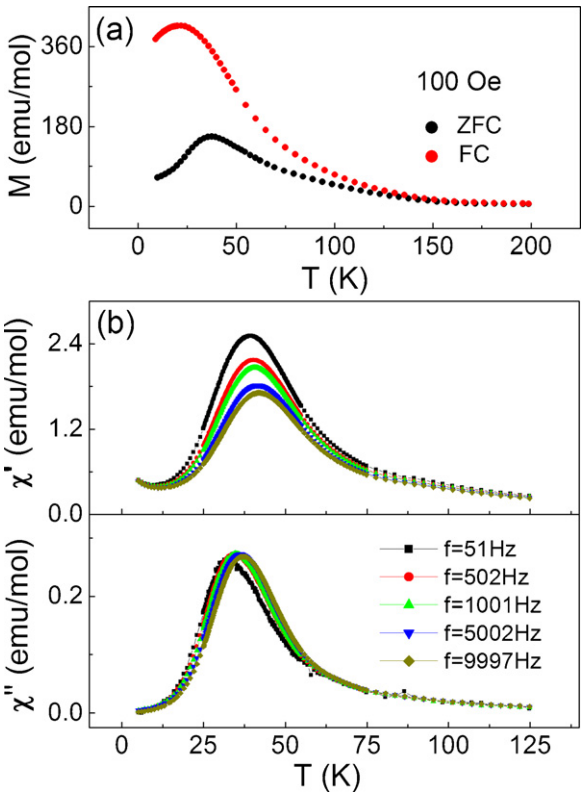

Fig. 1. (a) Temperature dependence of the dc magnetization after ZFC and FC measured at 100 Oe. (b) The temperature dependence of the in-phase and out-of-phase ac susceptibility for different frequencies 51, 502, 1001, 5002, 9997 Hz at a driving ac field of 5 Oe. All data were measured on heating.

behavior for the LSCO system was observed in the SG composition regime, especially for $La_{0.85}Sr_{0.15}CoO_3$ [11,17–19]. In this paper, to make a comparison with the well understood LSCO system, we presented a systematical study of magnetic properties in polycrystalline $Nd_{0.85}Sr_{0.15}CoO_3$ sample. The distinct feature of SG was noticed at low temperature and the signature of exchange bias (EB) effect gives the insight of the phase-separation scenario.

2. Experimental

The polycrystalline $Nd_{0.85}Sr_{0.15}CoO_3$ sample was prepared by conventional solid-state reaction. The stoichiometric mixture of high-purity Nd_2O_3, $SrCO_3$ and Co_2O_3 powders was thoroughly ground, fired in air at 1173 K for 48 h and slowly cooled to the room temperature (RT). The reacted powders were then cold pressed into pellets of thickness ~1 mm. Finally, these pellets were sintered at 1270, 1370 and 1470 K for 48 h, respectively, with intermediate grindings. X-ray diffraction (XRD) powder pattern was collected using the Bede D^1 XRD spectrometer with Ni-filtered Cu Kα radiation at RT. The result shows that the sample is single phase with orthorhombic structure (not shown). The dc magnetization and ac susceptibility measurements were carried out using the physical properties measurement system (PPMS-9T) of Quantum Design.

3. Results and discussion

Fig. 1(a) shows the temperature dependence of dc magnetization M (T) measured at 100 Oe with zero-field-cooled (ZFC) and field-cooled (FC) processes for $Nd_{0.85}Sr_{0.15}CoO_3$. It exhibits a broad onset of the increase below ~150 K in FC M (T) curve, which occurs at a temperature well below the point where the ZFC and FC M (T) curves bifurcate. Moreover, below the irreversible temperature a cusp in the ZFC M (T) curve is observed around 34 K. These characteristics are interpreted as the evidence of magnetic frustration and glassy behavior [20–22] or as being due to the measuring field much lower than the coercivity [19,23]. As seen in the FC M (T) curve,

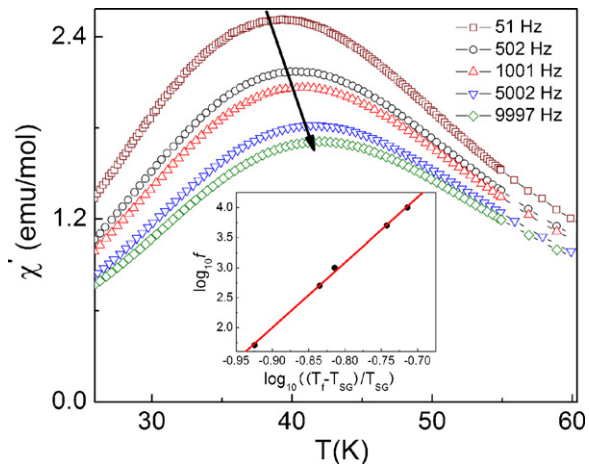

Fig. 2. Close up of the temperature dependence of the ac susceptibility at different frequencies. Inset shows $\log_{10}f$ vs $\log_{10}\left[\left(T_f - T_{SG}\right)/T_{SG}\right]$, demonstrating the agreement with Eq. (1). The solid line displays the best fitting results.

there is a subsequent decrease in magnetization below 21 K. This phenomenon can be imputed to the Nd ions coupled to the Co sublattice antiferromagnetically, which reduces the net magnetization as proven by Krimmel et al. [15]. Subsequently, we presented the temperature- and frequency-dependence of ac susceptibility measurement, a compatible technique way to search for glassy behavior in a material.

The in-phase and out-of-phase components of ac susceptibility vs temperature, i.e., $\chi'(T)$ and $\chi''(T)$, are displayed in Fig. 1(b). A frequency dependent maximum is observed. The peak value shifts toward higher temperature associated with the decrease in the magnitude of $\chi'(T)$ as frequency increasing. These peaks are close to the point where the ZFC magnetization shows a cusp around 34 K. The out-of-phase component of ac susceptibility also exhibits the similar frequency-dependence, as clearly as seen in Fig. 1(b). To judge the existence of glassy behavior in $Nd_{0.85}Sr_{0.15}CoO_3$, we tracked the frequency-dependence of the freezing temperature (T_f) considering the location of the peak maxima in $\chi'(T)$. A "close up" of these peaks of $\chi'(T)$ is shown in Fig. 2. The T_f dependence of frequency can be quite well described by the conventional critical "slow down" of the spin dynamics as [24]:

$$\frac{\tau}{\tau_0} \propto \left(\frac{T_f - T_{SG}}{T_{SG}}\right)^{-z\nu} \quad (1)$$

where τ is the measured relaxation time, τ_0 is the shortest relaxation time available to the system, T_{SG} is underlying SG transition temperature determined by the interaction in the system, z is the dynamical critical exponent, and ν is the critical exponent of the correlation length. The values of best fitting parameters obtained for $Nd_{0.85}Sr_{0.15}CoO_3$ are T_{SG} = 35.15 K, $\tau_0 = 1.69 \times 10^{-12}$ s and $z\nu$ = 10.86, respectively. As expected in the dynamic scaling theory, the value of T_{SG} is close to the location of the maximum in the ZFC M (T) curve. The value of $z\nu$ holds satisfactorily close to the limit found for classical SG compounds in the range of 4–12, and the value of τ_0 is reasonable close to the range 10^{-12}–10^{-14} s found for typical SG compounds [24–28]. Here, the larger characteristic time scale τ_0 is related to the nano-sized clusters of ferromagnetically coupled spins [12]. Therefore, the $Nd_{0.85}Sr_{0.15}CoO_3$ compound displays the characteristics of a SG. Nevertheless, as compared with $La_{0.85}Sr_{0.15}CoO_3$ (T_{SG} = 65 K) [11], the T_{SG} is lower for $Nd_{0.85}Sr_{0.15}CoO_3$. In contrast to the nonmagnetic La^{3+} ions, the magnetic ions Nd^{3+} contribute to the complicate magnetic interactions and competitions [15]. Meanwhile, due to the smaller ionic radius of Nd^{3+} (1.163 Å) in comparison with that of

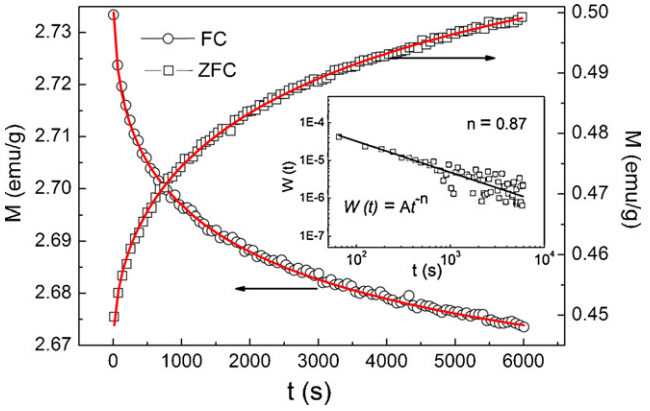

Fig. 3. Aging effect of ZFC and FC processes at 10 K, which exhibits perfectly mirror symmetry. Solid lines show the fitting data according to Eqs. (2) and (3), respectively. Inset shows the relaxation rate at 10 K after cooling field of 1000 Oe, and the solid line is the best fit to Eq. (4).

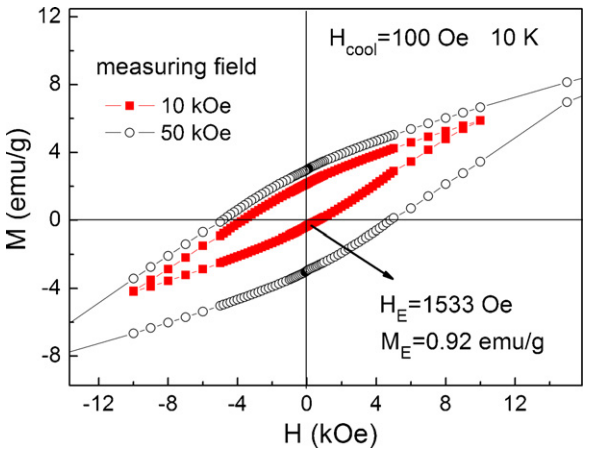

Fig. 4. Magnetic hysteresis loops at 10 K measured at different magnetic fields after field cooling in 100 Oe.

La^{3+} (1.216 Å), the crystal-field energy between the rhombohedral $La_{0.85}Sr_{0.15}CoO_3$ and orthorhombic $Nd_{0.85}Sr_{0.15}CoO_3$ is different, which induces different proportion of higher spin state of Co^{3+} [9,11,13,14]. Further theoretical and experimental work is needed to definitely resolve this issue.

We further performed time-dependent ZFC and FC magnetic relaxation measurements to reveal whether the system exhibits aging effect. The sample was cooled from 300 to 10 K at zero field. After a waiting time 2000 s, a dc magnetic field (H = 1000 Oe) was applied and the magnetization M was recorded vs time t, i.e., ZFC $M(t)$ aging progress, as shown in Fig. 3. Obviously, the magnetic moment increases monotonously with time. This magnetic relaxation curve $M(t)$ in SG system can be described by the stretched exponential form [10]:

$$M(t) = M_0 - M_r \exp\left[-\left(\frac{t}{\tau_r}\right)^{1-n}\right] \quad (2)$$

where M_0 refers to an intrinsic FM component, M_r and τ_r represent the glassy component depending on T and the waiting time, respectively, while n is only a function of T. It can be seen from Fig. 3 that the experimental data can be well fit to the Eq. (2), and the fitted parameter values are M_0 = 0.52 emu/g, $\tau_r = 10^{3.4}$ s and n = 0.41, respectively. We also measured the aging effect for $Nd_{0.85}Sr_{0.15}CoO_3$ with the FC procedure as following: the sample was cooled from 300 to 10 K at 1000 Oe. After waiting 2000 s, the magnetic field was switched off and the magnetization M was recorded vs time t. The magnetic moment decreases monotonously with time, as shown in Fig. 3. This aging curve $M(t)$ in SG system can be described by the exponential form [29]:

$$M(t) = M_0 \exp\left[-\left(\frac{t}{\tau}\right)^{n}\right] \quad (3)$$

It can be seen that the Eq. (3) can excellently describe the experimental data, and the fitted parameter values are M_0 = 0.087 emu/g, $\tau = 10^{3.4}$ s and n = 0.41, respectively. These fitted results confirm that the FC aging curve exhibits perfectly mirror symmetry with the ZFC one. This phenomenon illustrates that the SG behavior is the intrinsic property due to the frustrated spin magnetic structure induced by the spontaneous phase-separation in $Nd_{0.85}Sr_{0.15}CoO_3$.

The magnetic relaxation is analyzed to prove the nature of SG behavior, which has been used in LSCO [10] and some manganites [30]. According to Ulrich's model [31], for all magnetic particle densities the relaxation rate, $W(t) = -\left(d/dt\right)\ln M(t)$, decays by a power law with a density-dependent exponent n, which depends on the concentration and hence on the strength of the magnetic interaction, as following:

$$W(t) = At^{-n} \quad (4)$$

In $Nd_{0.85}Sr_{0.15}CoO_3$, the decay of $W(t)$ and n can be obtained from the best-fit curve shown in the inset of Fig. 3, and the fitted parameter value is n = 0.87, which is close to 1, suggesting the significant intercluster interaction. These results imply that the interaction among magnetic spins also makes contributions to the phase-separation and SG behavior in $Nd_{0.85}Sr_{0.15}CoO_3$.

The magnetic relaxation analyses of $Nd_{0.85}Sr_{0.15}CoO_3$ confirmed the SG phase at low temperature above, as determined on the basis of the ac susceptibility results. In the hole-doped perovskite cobaltite, $Nd_{0.85}Sr_{0.15}CoO_3$, the substitution of Sr on Nd sites introduces three kinds of magnetic interactions, namely, the FM double exchange between Co^{3+} and Co^{4+} ions, AFM superexchange interaction between Co^{3+}–Co^{3+} and Co^{4+}–Co^{4+} ions and the weak superexchange coupling of the Nd and Co sublattices. In this phase-separated perovskite oxide, it seems that the $Nd_{0.85}Sr_{0.15}CoO_3$ consists of FM clusters, non-FM regions, and SG regions that surround the FM clusters as interface layers between the FM regions and non-FM regions. As is well known, the proportion of coexisting phases can be influenced by the external field, particularly for the FM clusters and SG regions; while EB has often been observed in heterogeneous systems containing FM/AFM, FM/ferrimagnetic and FM/SG interfaces [32–35]. Therefore, it would be interesting to explore the EB effect at different measuring fields in this intrinsically phase-separated $Nd_{0.85}Sr_{0.15}CoO_3$ cobaltite. We measured the magnetic hysteresis loops of $Nd_{0.85}Sr_{0.15}CoO_3$ at 10 K for both the ZFC and FC processes under different measuring fields. A symmetric loop is inspected when the sample was cooled in ZFC condition (not shown here). When the sample was cooled to 10 K from 300 K at cooling field 100 Oe and the hysteresis loop was measured between ±10 kOe, an obvious negative horizontal and a positive vertical shifts of the loop are observed, as shown in Fig. 4 (solid circle), which are typical characteristics for the EB effect. The EB field H_E along the field axis and the magnetization shift M_E for the vertical axis are defined as $H_E = -\left(H_{right} + H_{left}\right)/2$ and $M_E = \left(M_{up} + M_{down}\right)/2$, respectively. The value of H_E is ≈1533 Oe, while the value of M_E is ≈0.92 emu/g. This suggests that the unidirectional anisotropy exists after the field cooling. The horizontal shift of the magnetic hysteresis loop can be attributed to the exchange coupling between the SG regions and the FM clusters, while the vertical shift may come from the incomplete reversal of the FM spins. However, unlike the conventional EB phenomenon, when

the $Nd_{0.85}Sr_{0.15}CoO_3$ sample was measured between ±50 kOe, the FC hysteresis loop does not show any shift, i.e., EB effect disappears at high magnetic field. Evidently, the signature of EB is attributed to the spontaneous separation between FM and SG phases in the compound [34]. In such a phase-separated system, the FM clusters grow up with increasing applied magnetic field, and the SG regions would be destroyed by an external field to some extent. It is the high magnetic field that influences the relative proportion of the coexisting phases. When the applied magnetic field increases to a certain value, the huge moments of the FM clusters cannot be pinned by the small portion of the SG spins. Consequentially, no exchange bias exists. These results imply that in the phase-separation system of $Nd_{0.85}Sr_{0.15}CoO_3$, the exchange coupling at the interfaces between the FM clusters and the SG regions may create an exchange anisotropy when the sample is cooled in a static magnetic field. The EB effect in $Nd_{0.85}Sr_{0.15}CoO_3$ sample further sustains the picture of the SG regions coexisting with FM and non-FM regions in such spontaneous phase-separation system.

4. Conclusions

In summary, the observed spin glassy behavior in the phase-separated $Nd_{0.85}Sr_{0.15}CoO_3$ cobaltite can be explained by the complicated interactions among Co^{3+}/Co^{4+} ions. The EB effects related to SG phase are also discussed. Particularly, unlike the conventional EB phenomenon, EB associated with phase-separation can be completely removed in a high measuring magnetic field owing to the variation of coexisting phases with increasing magnetic field.

Acknowledgements

This work is supported by the National Natural Science Foundation of China (Grant Nos. 50672019 and 10804024). The project was sponsored by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry. The project (HIT. NSRIF. 2009056) was supported by the Natural Scientific Research Innovation Foundation in Harbin Institute of Technology.

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