Observation of reentrant spin glass behavior in $LaCo_{0.5}Ni_{0.5}O_3$

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The magnetic and transport properties of $LaCo_{0.5}Ni_{0.5}O_3$ have been studied. The dc magnetization and the ac susceptibility studies suggest the presence of a magnetic-phase transition from a ferromagnetic (FM) to a spin glass phase at a low temperature. This type of reentrant spin-glass (RSG) behavior attached to a long-range ordered ferromagnet is observed in this system. A magnetoresistance of ∼10% is observed at 5 K which is unsaturated up to 11 Tesla suggests the presence of antiferromagnetic (AFM) interactions. It is likely that the competition between such AFM interactions with FM interactions yield an RSG phase.

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Spin glass (SG) is a system which lacks long-range-magnetic ordering. It originates from disorders, frustration of spins, or mixed interactions having both ferromagnetic (FM) and antiferromagnetic (AFM) interactions. In a random process, where a few FM interactions gets altered to AFM, the phase would still be FM but with some moments getting frustrated. If the existence of random AFM interactions increases beyond a threshold, frustration increases and long-range FM ordering is hindered, which in turn favors a spin glass phase.[1] Some materials reenters into a disordered state while cooling from an ordered state. When such a kind of transition exists, i.e., from FM/AFM to SG, where SG exists in lower temperatures, the system is a reentrant spin glass (RSG). In cobaltites such as $La_{1-x}Sr_xCoO_3$ (LSCO) with $x=0.5$, ferromagnetic and glassy behavior has been observed,[2,3] which was proposed to arise in the presence of both FM double-exchange interactions of Co^{4+}-Co^{3+} and AFM superexchange interactions of Co^{4+}-Co^{4+} and Co^{3+}-Co^{3+}. SG behavior was observed in cobaltites such as LSCO (with $x=0.09$[2] and 0.15[2,4]) and rare earth $(RE)Co_{0.7}Ni_{0.3}O_3$ (RE=La, Nd, and Sm).[5] The formation of spin glass in $LaCo_{0.7}Ni_{0.3}O_3$ is understood based on the competing FM and AFM interactions, which does not favor the formation of long-range ferromagnetism. The charge transfer between $Ni^{3+}+Co^{3+} \Leftrightarrow Ni^{2+}+Co^{4+}$ is promoted by the highly electronegative nature of Ni^{3+},[5] while ferromagnetism originates from Co^{3+}-Co^{4+} interactions.[6] The parent compounds $LaCoO_3$ and $LaNiO_3$ being diamagnetic and Pauli paramagnetic, respectively, it has been observed that SG state and the FM interactions are present only when Co and Ni exists together while no such observations were found when Co^{3+}/Ni^{3+} was replaced with a nonmagnetic ion, such as Ga^{3+}.[5]

In this article, we investigate $LaCo_{1-x}Ni_xO_3$ (LCNO) with $x=0.5$ which exhibits RSG behavior. To the best of our knowledge, among the existing oxide RSG systems, LCNO has the lowest difference between the ferromagnetic transition temperature (T_c) and spin glass freezing temperature (T_f). With sufficient experimental evidence, such as ac and dc magnetization, we suggest the presence of RSG nature in LCNO with $T_c \sim 52$ K and $T_f \sim 24$ K.

Our samples were prepared by conventional solid-state synthesis using La_2O_3, Co_3O_4, and NiO. The sample was heated at 1300 °C with a few intermediate grindings. Iodometric titration was done to estimate oxygen content and was found to be stoichiometric.

The ac susceptibility measurements were done at various frequencies ranging from 15 Hz to 1 KHz, at an applied field $H_{ac}=178$ mOe. From the in-phase component (χ') of the susceptibility, a peak was observed at $T \sim 52$ K which had no frequency dependence. This being a characteristic nature of ferromagnetic ordering, interestingly a shoulder was observed at $T \sim 22$ K. This shoulder exhibited a clear shift with varying the applied frequency indicating the presence of a glassy nature as shown in Fig. 1(a). The changes observed in the shoulder were prominent in the out-of-phase component (χ'') as shown in Fig. 1(b). This reveals the existence of spin frustrations. The freezing temperature for RSG at low temperature and the ferromagnetic transition temperature at ∼52 K shall be denoted as T_f and T_c, respectively. The maximum change in the freezing temperature, ΔT_f is denoted as $\Delta T_f(\omega)=(T_f^{1\ \mathrm{KHz}}-T_f^{15\ \mathrm{Hz}})$ and it is ∼5 K, where $T_f^{1\ \mathrm{KHz}}$ and $T_f^{15\ \mathrm{Hz}}$ represents T_f at 1 KHz and 15 Hz, respectively. A quantitative assessment of ΔT_f with respect to ω is given by $\Delta T_f/[T_f\Delta(\log(\omega))]$ and is found to be 0.095. This value is

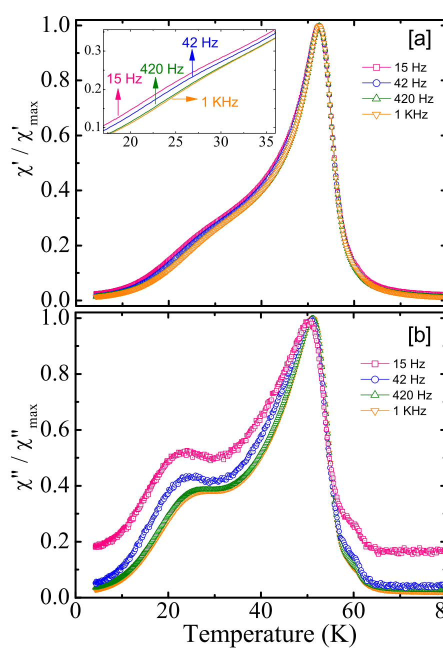

FIG. 1. (Color online) Temperature dependence of χ_{ac} (a) In-phase component and (b) out-of-phase component at various frequencies at $H_{ac}=178$ mOe. Inset of (a): clear view of χ'.

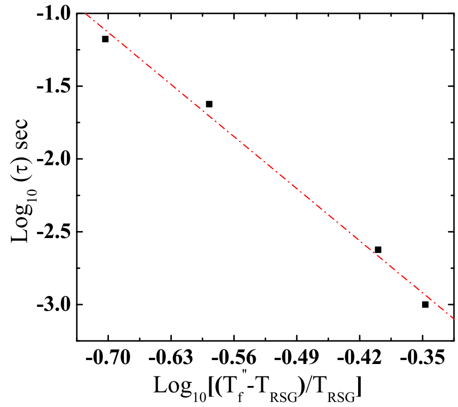

FIG. 2. (Color online) Dependence of τ with $\log_{10}[(T_f''-T_{RSG})/T_{RSG}]$. The values obtained are $T_{RSG}=19.8\pm0.7$ K; $z\nu=5.32\pm0.6$; and $\tau_o=(1.5\pm0.2)\times10^{-5}$ s.

comparable to that obtained in other spin glass systems.[7] Earlier studies on LCNO[8] have reported a shoulder and a peak in χ' but detailed analysis were not performed.

Dynamical scaling analysis was performed using the relation $\tau/\tau_o=[(T_f''-T_{RSG})/T_{RSG}]^{-z\nu}$, where T_f'' is the freezing temperature (from out-of-phase component). From this analysis, the spin flipping time (τ_o), critical exponent ($z\nu$), and the critical temperature for reentrant spin glass ordering (T_{RSG}), i.e., T_f'' at $f\to0$ are determined to be $(1.5\pm0.2)\times10^{-5}$ sec, 5.32 ± 0.6, and 19.8 ± 0.7 K, respectively. Figure 2 shows the dependence of τ with $[(T_f''-T_{RSG})/T_{RSG}]^{-z\nu}$. Although $\tau_o\sim10^{-13}$ sec for a SG, the higher value of τ_o indicates the spin flipping to be slower. Such kind of higher values have been observed elsewhere in SG[9,10] and RSG.[11] Regardless of these observations, the reasons behind such longer flipping time are still unclear and are under investigation. In general, determining the T_f for RSG is less accurate when compared to SG.[12]

Further investigations on ac susceptibility measurements were proceeded with superimposed dc magnetic field, i.e., with $H_{ac}=178$ mOe and $H_{dc}=63$ Oe. In case of a ferromagnet, the magnitudes of both $\chi'(\omega)$ and $\chi''(\omega)$ decreases drastically in the presence of dc magnetic fields. But in the case of a spin glass, the behavior is unlike a ferromagnet, i.e., the changes in the magnitudes of $\chi'(\omega)$ and $\chi''(\omega)$ are minor. For RSG systems, $\chi'(\omega)$ and $\chi''(\omega)$ experiences a drastic change in the FM phase while the changes are feeble at the SG phase. Similar to FM, in case of RSG, the T_f shift towards lower temperatures. These observations have been found in other RSG systems.[12] This could be observed from the change in the ratio of $\chi'(T_f)/\chi'(T_c)$ and $\chi''(T_f)/\chi''(T_c)$. Figures 3(a) and 3(b) show $\chi'(\omega)$ and $\chi''(\omega)$, respectively with H_{ac}, when the superimposed $H_{dc}=0$ and 63 Oe. Such kind of change in the ratio influenced by the applied H_{dc} gives a clear representation of RSG behavior in LCNO. For LCNO ($x=0.6$), a shoulder was observed ~55 K. Though the reasons are still unclear, this effect was believed to be due to the Ni sublattice.[13] Although no such effects were observed in our dc magnetization data, a little kink is observed ~60 K in the χ'' of ac susceptibility, which had no frequency dependence. Such kind of a kink is absent in case of χ'. The kink is absent in the χ'' data when a dc field is superimposed.

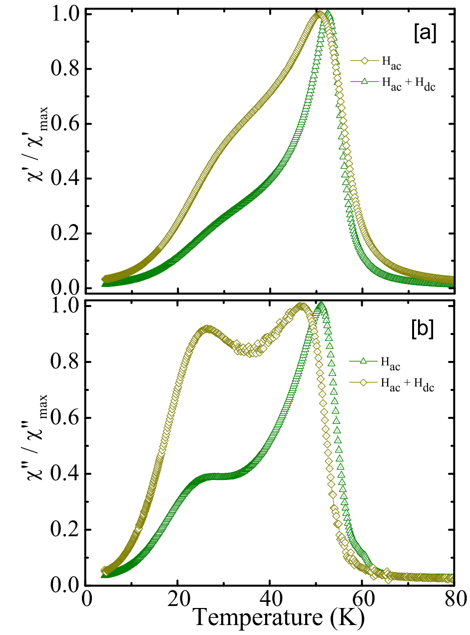

FIG. 3. (Color online) Influence of $H_{dc}=63$ Oe along with $H_{ac}=178$ mOe at $f=420$ Hz (a) In-phase component and (b) out-of-phase component.

Temperature-dependent dc magnetization of LCNO in zero-field-cooled (ZFC) and field-cooled (FC) modes measured with a SQUID magnetometer with 100 Oe magnetic field, i.e., ($T=5$ to 300 K) is shown in Fig. 4. The declination in the FC magnetization at low temperature can be attributed to the SG nature. The ZFC magnetization experiences a sharp cusp, and unlike a ferromagnet, the FC magnetization does not exhibit "Brillouin-like" behavior, while still the bifurcation between FC and ZFC is observed. All these observations are attributable to the rudimentary qualities of spin glass nature. In this case the temperature of irreversibility, T_{irr} was observed ~55 K. The declination in the χ_{FC} at $T\sim25$ K, indicates the existence of frustrated spins at the expense of long-range ordering while long-range FM ordering is present ~25 K $\leq T\leq$ 55 K. In our earlier studies,[14] FC and ZFC indicated that magnetic anisotropy is responsible for the difference between $\chi_{ZFC}(T)$ and $\chi_{FC}(T)$ which could have happened if the spins are oriented by an

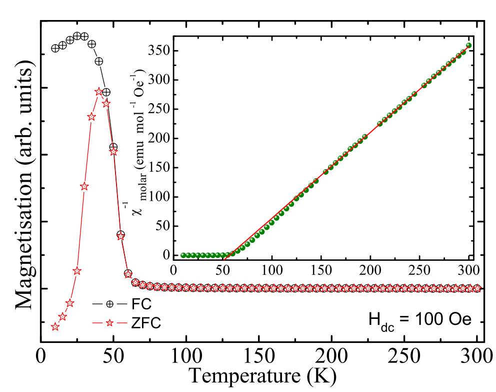

FIG. 4. (Color online) Temperature dependence of FC and ZFC magnetization at $H_{dc}=100$ Oe. Inset shows the inverse of χ_{dc}.

TABLE I. Calculated spin-only moments (μ_{so}) for the possible spin-state configurations in $LaCo_{0.5}Ni_{0.5}O_3$. "*" indicates the compatibility of possible spin states with experimental results.

Spin-state configurations	Spin-only moments (μ_{so}) μ_B
$Co^{3+}(S=0), Ni^{3+}(S=1/2)$	1.2247
$Co^{3+}(S=1), Ni^{3+}(S=1/2)$	2.3452*
$Co^{3+}(S=2), Ni^{3+}(S=1/2)$	3.6742
$Co^{3+}(S=0), Ni^{3+}(S=3/2)$	2.7386
$Co^{3+}(S=1), Ni^{3+}(S=3/2)$	3.3911
$Co^{3+}(S=2), Ni^{3+}(S=3/2)$	4.4158
$Co^{4+}(S=1/2), Ni^{2+}(S=1)$	2.3452*
$Co^{4+}(S=3/2), Ni^{2+}(S=1)$	3.3911
$Co^{4+}(S=5/2), Ni^{2+}(S=1)$	4.6368

applied field or by their anisotropy along energetically favored directions when the sample is cooled from higher temperatures. In earlier studies,[15] LCNO has been reported to be ferromagnetic (for $x \geq 0.2$). But actually carefully looking into their results of $\chi_{ZFC}(T)$ and $\chi_{FC}(T)$ it is understood that spin glass nature is present.

In order to find the type of long-range magnetic ordering, the inverse of χ_{dc} is examined and is shown as an inset of Fig. 4. The effective paramagnetic moment (μ_{eff}) calculated from the inverse of χ_{dc} is found to be $2.33\mu_B$ while the Curie constant and the Weiss temperature (Θ) were determined to be 0.68 emu mol^{-1} K^{-1} and $\sim$56.6 K, respectively. The obtained value of Curie constant suggests that the spins can be attributed either to Co^{3+} (Intermediate Spin, t_{2g}^5 e_g^1)—Ni^{3+} (Low Spin, t_{2g}^6 e_g^1), or to Co^{4+} (Low Spin, t_{2g}^5 e_g^0)—Ni^{2+} (t_{2g}^6 e_g^2). The possible spin-state configurations and their spin-only moments (μ_{so}) are shown in Table I. The positive value of Θ suggests that the long-range ordering present is ferromagnetic in nature. Comparing the dc with ac susceptibility details, the temperature at which χ_{max}(FC) being similar to T_f, while being located far away from T_{irr}, could be attributable to RSG phenomena.

Electrical behavior of LCNO is verified to be of semiconducting nature as reported earlier.[15] Temperature-dependent magnetoresistance, i.e., MR(T) has been measured for $5 \leq T \leq 300$ K with $H=11$ Tesla and the field-dependent magnetoresistance, i.e., MR(H) has been measured up to 11 Tesla at 5 K as shown in Fig. 5. We observe a negative MR and is observed to increase rapidly as the temperature is reduced. No anomaly was observed both at the FM and RSG regions. A maximum of $\sim$10% of negative MR was observed at 11 Tesla. It has been shown previously that, in LCNO when x increases from 0.25 to 0.45, the tendency of MR to saturate is reduced.[16] In fact, this is found to be true for $x=0.5$ as well, where it is unsaturated till 11 Tesla. This explains the

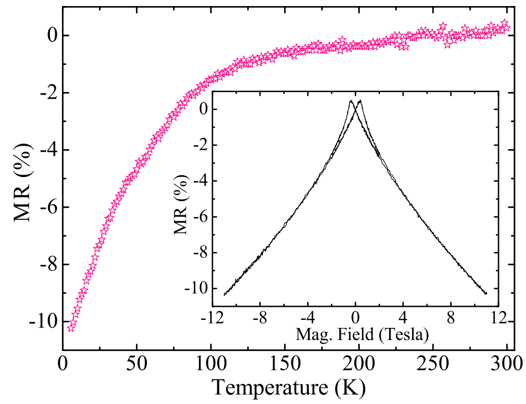

FIG. 5. (Color online) Temperature dependence of MR ARNING $[(R_{11T}-R_{0T})/R_{0T}]$. Inset showing the field dependence of MR at 5 K.

presence of AFM interactions arresting the saturation of MR even at high magnetic fields.[16] Despite no clear mechanism being available to explain the cause of negative MR in LCNO, such effects could be due to the realignment of magnetic moments to exhibit higher probability of electron hopping. But among the existing hopping mechanisms, such as variable range hopping (VRH), Efros-Shklovskii VRH, polaron hopping, and thermally activated transport, LCNO ($x \geq 0.4$) followed none of them.[15] Thus, the reduction in resistance on the application of magnetic fields could originate collectively from (i) decrease in spin-disorder scattering, (ii) growth of the domains giving rise to better metallic path, as explained by double exchange mechanism where metallic conduction is coupled with FM interactions, (iii) increase in mean-free path of electrons, and (iv) growth of domains in applied field giving rise to decrement in the probability for domain-wall scattering. Though it has been suggested earlier[5] that the onset of negative MR and freezing temperature are linked together, such an observation was contradicted later.[16] Our results are in support of the later since we find no association between them.

Although SG, glassy FM behavior has been observed in cobaltites, we have shown that LCNO ($x=0.5$) exhibits RSG phenomena. Though earlier studies have reported LCNO to be ferromagnetic (for $x \geq 0.2$), detailed studies of the ac and dc magnetization reveals the presence of RSG in LCNO. We have also evaluated the magnetotransport properties of LCNO exhibiting negative MR. The unsaturated behavior of MR suggests the presence of the AFM interactions, which could be responsible to compete with FM interactions in resulting the moments to dwell frustrated.

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