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Magnetic properties in polycrystalline and single crystal Ca-doped $LaCoO_3$

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Polycrystalline (PC) and single crystalline (SC) Ca-doped $LaCoO_3$ (LCCO) samples with the perovskite structure were synthesized by conventional solid-state reaction and the floating-zone growth method. We present the results of a comprehensive investigation of the magnetic properties of the LCCO system. Systematic measurements have been conducted on dc magnetization, ac susceptibility, exchange-bias, and the magnetocaloric effect. These findings suggest that complex structural phases, ferromagnetic (FM), and spin-glass/cluster-spin-glass (CSG), and their transitions exist in PC samples, while there is a much simpler magnetic phase in SC samples. It was also of interest to discover that the CSG induced a magnetic field memory effect and an exchange-bias-like effect, and that a large inverse irreversible magnetocaloric effect exists in this system. © *2011 American Institute of Physics*. [doi:10.1063/1.3562518]

Currently, there is an ongoing debate and increased research intensity on the magnetism of the $LaCoO_3$ (LCCO) system, due to the fascinating properties of compounds in this family and possible multifunctional applications.[1–6] The main controversial points are concerned with the spin states (low to intermediate/high spin), magnetic behaviors [phase separation and spin glass (SG) state], and transitions between them. It is commonly accepted that the ground state of $LaCoO_3$ is a nonmagnetic insulator. It is commonly considered that with increasing temperature a paramagnetic insulating state continuously develops above 50 K and an insulator-to-metal transition is observed around 500 K.[7] There has been controversy on the nature of the high-temperature spin state, namely, whether it is high-spin (HS), intermediate-spin (IS), or even a mixture of both.[8]

The $La_{1-x}Ca_xCoO_3$ system has been studied by many groups.[8–17] The substitution of Ca^{2+} on La^{3+} oxidizes part of the Co^{3+} into Co^{4+}. The spin configuration of Co^{4+} has been proposed by different investigators to be LS ($t_{2g}^5e_g^0$, $S=1/2$), HS ($t_{2g}^3e_g^2$, $S=5/2$), and even IS ($t_{2g}^4e_g^1$, $S=3/2$), depending on the Ca content and temperature.[6,8] The theoretical effective magnetic moment (μ_{eff}) of Co^{3+} and Co^{4+} in the LS, IS, and HS states are 0, 2.83, and 4.90 μ_B and 1.73, 3.87, and 5.92 μ_B, respectively.[11–17]

Since the magnetic and electrical properties of rare earth transition metal oxides with perovskite structure are strongly dependent on the valence state and spin state of the metal ions, and the defects, these make the materials' magnetic properties very sensitive to sample preparation conditions and processing. It will be worthwhile to compare the properties of a single crystalline (SC) sample with bulk polycrystalline (PC) samples prepared by the conventional solid-state reaction method. In the present work, we have prepared PC and SC LCCO with the same composition of starting raw powders, determined the magnetic properties, and analyzed the differences between these two types of samples. Interestingly, anomalous magnetic field memory effect, exchange-bias-like effect, and a large inverse irreversible magnetocaloric effect have been observed in this system. We propose that compositional inhomogeneity are the predominant source of the magnetic properties.

PC and SC $La_{0.7}Ca_{0.3}CoO_3$ (LCCO) samples with the perovskite structure were synthesized by conventional solid-state reaction and the floating-zone growth method. The crystal structure analysis was performed by x-ray diffraction (XRD). The magnetization measurements were performed using a physical properties measurement system (PPMS, 14 T) in the temperature range of 5–300 K. The entropy change was evaluated from the magnetization isotherms.

Microstructure analyses was conducted by XRD, and neutron diffraction, and they have confirmed the high purity and perovskite structure in the samples. XRD and Rietveld refinement results on $La_{0.7}Ca_{0.3}CoO_3$ (LCCO) PC samples (not shown here) indicate that the PC sample has the mainly orthorhombic (space group: *Pnma*) phase (*O* phase) with a small amount of rhombohedral (space group: *R*-3*c*) (*R* phase), while the SC sample has the mainly *O* phase with a little more amount of *R* phase (than PC sample), which were due to the different loss amount of Ca content during the sample preparation.[6–8]

The temperature dependence of the zero-field-cooled (ZFC) and field-cooled (FC) magnetization was measured for both PC powder and single crystal (SC) samples. For all the results on the present SC sample of this paper, the applied fields were parallel to the *c*-axis. The results are replotted as dc susceptibility and inverse susceptibility in Figs. 1(a)–1(d). A sharp increase in the magnetization occurs

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in the low-field FC data around the Curie temperature $T_C \approx 106$ K for both poly- and single-crystal samples, indicating that the system has become ordered and attained a spontaneous magnetization. A characteristic strong irreversibility between the low-field ZFC and FC magnetization curves appears just below the transition temperature. It is suggested that this irreversibility possibly arises due to the canted nature of the spins or due to the random freezing of spins. The single-crystal sample shows much simpler transitions compared to the PC ones, while the ZFC curve shows only one similar peak around 90 K [Fig. 1(c)]. At high temperatures (higher than T_C), there may be a first order structural phase transition at temperature, $T_{ST} \approx 250$ K [Fig. 1(a) and 1(b)] for the PC sample, and $T_{ST} \approx 160$ K [Fig. 1(c) and 1(d)] for the single-crystal sample, which are induced by the spin state changes (from lower spin state to higher spin state), since the slope of the $1/\chi - T$ curves is changed and the effective magnetic moment (m_{eff}) increases after transition [Fig. 1(b) and 1(d)]. Above the transition temperature, both samples show Curie–Weiss behavior, and a fit to the Curie–Weiss law yields a FM μ_{eff}, the values of which are listed in Figs. 1(b) and 1(d).

Although ferromagnetic (FM) interactions dominate the magnetic transitions, AFM interactions also exist between Co ions. This is because the system phase may separate into hole-rich FM clusters dominated by the FM double exchange interaction between Co^{3+} and Co^{4+}, with the clusters embedded in a hole-poor non-FM matrix. This matrix is dominated by the Co^{3+}–Co^{3+} interaction, which is known to be AFM superexchange, as with the Co^{4+}–Co^{4+} interaction. The coexistence of and competition between FM and AFM interactions could lead to SG-like behavior. Crystallographic inhomogeneity, stoichiometric inhomogeneities, and the Co ion spin-state transitions heighten the coexistence of the FM and AFM interactions, and bring about magnetic phase separation in the samples, which similar as Sr-doped system.[17] It is highly probable that the crystallographic homogeneity and the stoichiometric homogeneities in the PC sample are much lower than in the SC sample, which leads to much more complex magnetic behaviors in the PC sample.

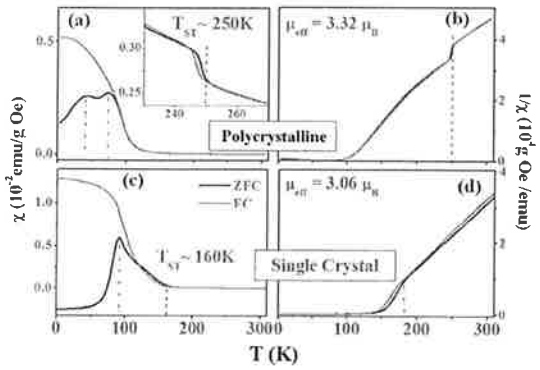

FIG. 1. (Color online) dc and inverse susceptibility (χ and $1/\chi$) vs T curves under zero-field cooling (ZFC) and after field cooling (FC) at a field of 1 kOe for the PC sample (a) $\chi - T$, (b) $1/\chi - T$ and for the SC sample (c) $\chi - T$, (d) $1/\chi - T$.

M-H loops were collected at different temperatures under ZFC and FC with different sweep fields. A large hysteresis loop develops below T_C (106 K) and attains a larger remanence value (M_R) and higher coercive force (H_C) at the lowest temperature. The material becomes harder with decreasing temperature, with the coercive field increasing monotonically with decreasing temperature. The difference between PC and SC samples is that the loops or curves of the SC sample appear straighter and show sharp changes in all the figures, while all the values of M_R and H_C for the SC are larger than the corresponding PC ones.

In Fig. 2, we show M-H loops of PC [(a) and (b)] and SC [(c) and (d)] samples after ZFC and 1.5 T FC to 5 K. We have used different sweep fields of 1, 5, 10, 20, and 50 kOe in the M-H loop measurements after both ZFC and 1.5 T FC cooling. We have selected the 10 and 20 kOe sweep field loops as examples, and they are shown in Fig. 2. It is interesting to note that, in the left panels, Figs. 2(a) and 2(c), for sweep field of 1 T, less than the field cooling field of 1.5 T, the ZFC M-H loops were closed, while the FC M-H loops were not closed and were upshifted. The nonclosed loop phenomenon is typical SG relaxation behavior, while the upshifts are mainly due to the FM M_R behavior. We suggest that the SG or more likely here, the cluster spin glass (CSG), has also significantly contributed to the upshifts or downshifts. In the right panels, Figs. 2(b) and 2(d), for a sweep field of 2 T, greater than the field cooling field of 1.5 T, both the FC and ZFC M-H loops were closed, but the M-H loops were still up/downshifted, with the values lower than the left panel ones. The up/downshifts of the M-H loops are attributed to exchange bias-like behavior (M_{EB}), and the values of M_{EB} are listed in Fig. 2. Moreover, the left-/right-shift the of M-H loops is attributed to exchange bias (H_{EB}), and the values of H_{EB} are listed in Figs. 2(b) and 2(d). For the origin of the exchange bias, we note that the authors of Ref. 18 have observed similar shifts on both axes, representing exchange-bias-like phenomena, and there are later arguments on it,[19] however, our results suggest that, excepting the minor hysteresis loops, the

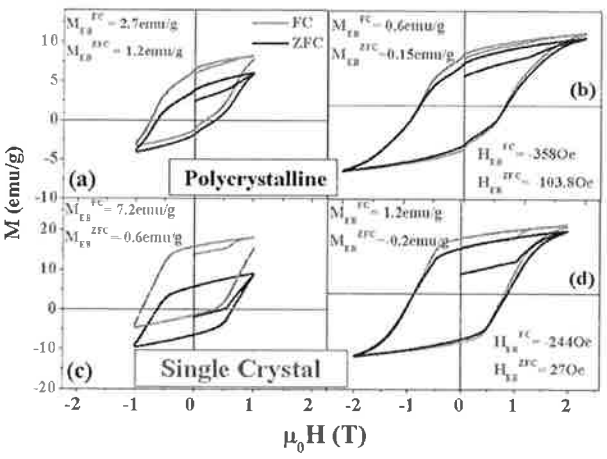

FIG. 2. (Color online) M-H loops of $La_{0.7}Ca_{0.3}CoO_3$ PC [(a) and (b)] and single-crystal [(c) and (d)] samples after ZFC and 1.5 T FC to 5 K. Different sweep fields were used, lower or higher than the cooling field of 1.5 T, and showed different loop shifting features, representing exchange-bias-like phenomena.

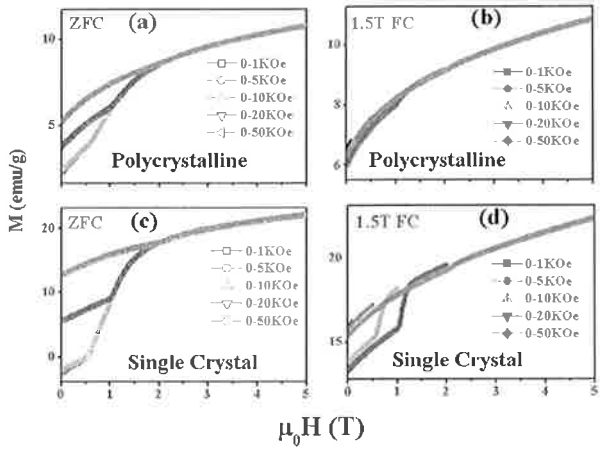

FIG. 3. (Color online) *M-H* curves of $La_{0.7}Ca_{0.3}CoO_3$ polycrystalline [(a) ZFC, (b) FC] and single-crystal [(c) ZFC, (d) FC] samples with different sweep fields after ZFC and 1.5 T FC to 5 K. Different magnetic field-memory effects were observed after ZFC and 1.5 T field cooling.

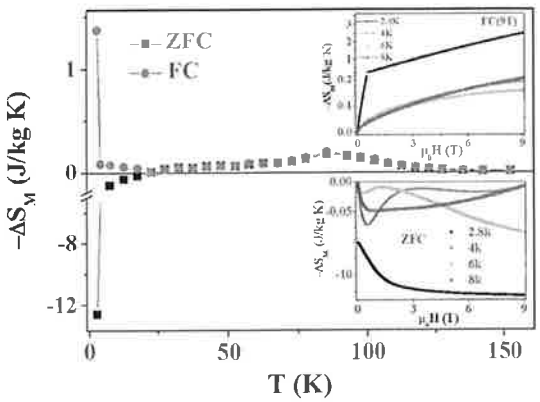

FIG. 4. (Color online) Magnetic entropy changes ($-\Delta S_M$) versus temperature curves for 0 to 1.5 T field change. The upper and lower insets show $-\Delta S_M - H$ curves at 2.8, 4, 6, and 8 K under field changes of 0 to 9 T after ZFC and 9 T field cooling to 2.6 K for the PC sample.

freezing properties of local anisotropy in a CSG system make a significant contribution to both shifts. Moreover, the grain boundaries in PC samples can enhance the exchange bias, so that the H_{EB} in the PC sample [in Fig. 2(b)] $> H_{EB}$ in the single-crystal sample [in Fig. 2(d)], even though the H_C of the PC sample is less than H_C of the SC sample.

In Fig. 3, we show magnetization (*M-H*) curves of PC [(a) ZFC, (b) FC] and single-crystal [(c) ZFC, (d) FC] samples measured with different sweep fields after ZFC and 1.5 T FC to 5 K. Different magnetic field-memory effects were observed after ZFC and 1.5 T field cooling. It should be noted that all the curves exhibit a kink or step in the *M-H* curves, with the field position the same as the maximum field value of the last sweep field. For the ZFC *M-H* curves in the left panels of Figs. 3(a) and 3(c), the kinks or the steps are increased step by step with increasing sweep field. For the *M-H* curves after 1.5 T FC in the right panels of Figs. 3(b) and 3(d), the kinks are increased step by step with increasing sweep field, but the steps go down when the sweep field is less than the 1.5 T FC field, but increase back up to the first field sweep M_R level when the sweep field $>$ 1.5T FC field. These demonstrate the feature of that, the kink value (field value) always coincides (remembers) with the last front maximum sweep field value—we define it as the magnetic field memory effect. This effect is possibly due to a combination of hard FM typical clusters showing SG behavior and frozen spin behavior.

We also conducted isothermal magnetization measurements of the PC sample at temperatures from 2.6 to 160 K, then evaluated the magnetic entropy change ($-\Delta S_M$) under ZFC and FC to 2.6 K from the calculated isothermal magnetic entropy change $-\Delta S_M$ from isothermal magnetization curves according to $\Delta S_M(T,P,H)_{\Delta H,P} = \int_{H_1}^{H_2}[\partial M(T,P,H)/\partial T]_{H,P}dH$. We found that the frozen spins have a significant influence on the $-\Delta S_M$. An interesting result is presented in Fig. 4, where the $-\Delta S_M - T$ curves in the low temperature range show totally different features between the ZFC and FC cooling procedures. $-\Delta S_M$ shows a very large inverse irreversibility value for the ZFC process, since there are a large amount of unfrozen spins aligned under the external field in the low temperature range, while $-\Delta S_M$ shows a normal positive value and a slightly larger $-\Delta S_M$ value at 2.8 K, which indicates that a small amount unfrozen spins still exist. This is shown more clearly in the upper and lower insets in Fig. 4. The $-\Delta S_M - H$ curves at 2.8, 4, 6, and 8 K under field changes of 0 to 9 T after ZFC to 2.6 K show more complex behavior than the FC ones.

We have demonstrated several types of complex and fascinating magnetic behavior in the LCCO system, which will possibly be useful for multifunctional applications. The magnetic properties in this system strongly depend on the sample preparation processing and conditions. From comparing the magnetic behaviors in PC and SC samples, we propose that the compositional inhomogeneity (mainly Ca^{2+} content) lead to complex variations in the Co ion valence and spin states, which then lead to the strong spin-glass/cluster-spin-glass behavior which significantly influences the magnetic properties of this system.

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