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Field-induced crossover from cluster-glass to ferromagnetic state in La$_{0.7}$Sr$_{0.3}$Mn$_{0.7}$Co$_{0.3}$O$_3$

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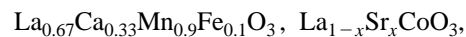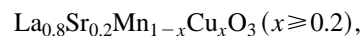
The thermodynamics and kinetics of the magnetic states of the semiconductor-like compound La$_{0.7}$Sr$_{0.3}$Mn$_{0.7}$Co$_{0.3}$O$_3$ were studied by detailed magnetic measurements. The spontaneous magnetic state was found to be a cluster-glass phase which can cross over to a ferromagnetic state under an external magnetic field H. The defreezing temperature T_f for the cluster-glass phase and the merging temperature T_m for zero field cooled and field cooled magnetizations are related to the field H by $H_j = H_{0j}(1 - T_j/T_c)^{n_j}$, where H_{0j} and n_j are constants and $j = f, m$. Codoping tends to destroy the double exchange in Mn^{4+}–O–Mn^{3+} and broadens the coexistence region of the cluster-glass and ferromagnetic states. The magnetic relaxation was found to deviate from the usual logarithmic time dependence and follow a power law. © *1999 American Institute of Physics.*
[S0021-8979(99)09703-0]

I. INTRODUCTION

The hole-doped manganese and cobalt oxides, such as La$_{1-x}$M$_x$MnO$_3$(M=Ca,Sr) and La$_{1-x}$M$_x$CoO$_3$ with colossal magnetoresistance (CMR) have attracted considerable attention during the last few years. It is known that the doping of a bivalent element M can lead to a mixed valency of the transition metal ions (Mn and Co ions), which is responsible for the double-exchange (DE) interaction in Mn^{4+}–O–Mn^{3+} or Co^{4+}–O–Co^{3+}. Recent theoretical and experimental studies on this class of materials indicate that the effects of polaron as well as DE interaction are required for the understanding of the unusual transition and transport mechanism.[1–5] Previous investigations on the La$_{0.7}$Ca$_{0.3}$Mn$_{1-x}$Co$_x$O$_3$ ($0.05 \leq x \leq 0.5$) system have shown that the DE interaction and the metallic state are very ''fragile.'' The substitution of Co for Mn makes the DE interaction of Mn^{4+}–O–Mn^{3+} short ranged, and hence even a small amount of Co substitution can destroy the ferromagnetic (FM) order.[6,7] Since the DE interaction is ferromagnetic and the superexchange interaction between ions of the same valence state is antiferromagnetic,[6] at temperatures below T_c the spontaneous magnetic state may not have a long-range order, and hence a cluster-glass (CG) or spin-glass (SG) state is formed. CG or SG behaviors were observed in perovskites with or without metal-insulator transition and CMR effect,[8–11] such as in

La$_{0.8}$Sr$_{0.2}$Mn$_{1-x}$Cu$_x$O$_3$ ($x \geq 0.2$),

La$_{(2-x)/3}$Ba$_{(1+x)/3}$Mn$_{1-x}$Cu$_x$O$_3$ ($x \geq 0.3$),

La$_{0.67}$Ca$_{0.33}$Mn$_{0.9}$Fe$_{0.1}$O$_3$, La$_{1-x}$Sr$_x$CoO$_3$,

and

La$_{1-x}$Sr$_{1+x}$MnO$_4$ ($x \geq 0.2$).

Despite the fact that there have been some previous studies on Co-substituted systems,[6,7] the magnetic field-induced effects on the thermodynamics and kinetics of the magnetic states are still unclear. This is especially so for the La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Co$_x$O$_3$ system. The magnetic phase diagrams for manganese and cobalt oxides, which are fundamentally different in many aspects,[12–17] are expected to be rather complex and need further clarification.

In order to study the magnetic characteristics of CMR compounds, the La$_{0.7}$Sr$_{0.3}$Mn$_{1-x}$Co$_x$O$_3$ system is a good candidate because Co has a special spin state. In this article, the zero field cooled and field cooled magnetization and relaxation behaviors of polycrystalline La$_{0.7}$Sr$_{0.3}$Mn$_{0.7}$Co$_{0.3}$O$_3$ are presented.

II. EXPERIMENT

The sample La$_{0.7}$Sr$_{0.3}$Mn$_{0.7}$Co$_{0.3}$O$_3$ was prepared by a standard solid state reaction method. The appropriate mixture of La$_2$O$_3$ (99.9%), SrCO$_3$ (99%), Co$_2$O$_3$(99.99%), and Mn$_2$O$_3$ (99.99%) was ground and calcined at 1100 °C in air

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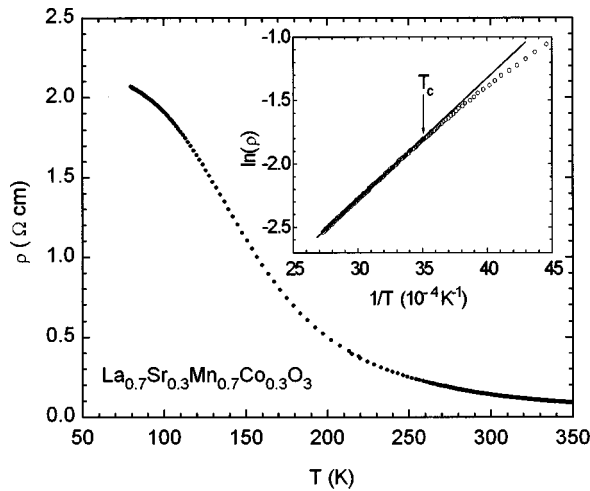
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FIG. 1. Temperature dependence of the resistivity of $La_{0.7}Sr_{0.3}Mn_{0.7}Co_{0.3}O_3$. The inset shows that at temperature above 285 K the resistivity follows a thermally activated behavior. The dots are experimental data and the solid line is the fit based on $\rho(T)=\rho_0 \exp(E_g/k_BT)$.

for 48 h. The reactant was reground and pressed into pellets for sintering at 1350 °C for 48 h. Powder x-ray diffraction patterns were recorded by a Rigaku D/Max-B diffractometer using Cu$K\alpha$ radiation. It was found that the sample $La_{0.7}Sr_{0.3}Mn_{0.7}Co_{0.3}O_3$ is single phase with rhombohedrel structure. The magnetization was measured in both zero field cooled (ZFC) and field cooled (FC) states with different measuring fields ranging from 10 to 10^4 Oe using a commercial superconducting quantum interference device magnetometer. For the measurement of the magnetization relaxation, the sample was initially cooled in zero magnetic field from above T_c to the measuring temperature. A magnetic field of 1000 Oe was then applied and the relaxation data were collected. The resistivity was measured by a standard four-probe method.

III. RESULTS AND DISCUSSION

The temperature dependence of the resistivity depicted in Fig. 1 indicates that the sample is semiconductor-like, which is different from those of $La_{0.7}Sr_{0.3}MnO_3$ and $La_{0.7}Sr_{0.3}CoO_3$. This implies that the partial Co doping can change the transport property and destroy the DE interaction of Mn^{4+}–O–Mn^{3+} as a result. The inset of Fig. 1 shows that at temperatures above 285 K the resistivity can be fitted to $\rho(T)=\rho_0 \exp(E_g/k_BT)$ with a transport energy gap $E_g=82$ meV, which is of the same order of magnitude as for $La_{1-x}Ca_xMnO_3$.[18] Below 285 K the resistivity of the sample is lower than that expected from the resistivity calculated using the thermally activated type temperature dependence, which can be regarded as the occurrence of some kind of spin ordering. In the following experiments, one can see that the Curie temperature T_C is about 285 K.

Figure 2 shows the variations of the magnetizations with temperature in magnetic fields of 10 and 1000 Oe for $La_{0.7}Sr_{0.3}Mn_{0.7}Co_{0.3}O_3$. In the FC curves, M_{FC} decreases continuously with increasing temperature, which gives a FM to paramagnetic (PM) transition T_c of 285 K. However, in the ZFC curves, M_{ZFC} increases to its maximum value at
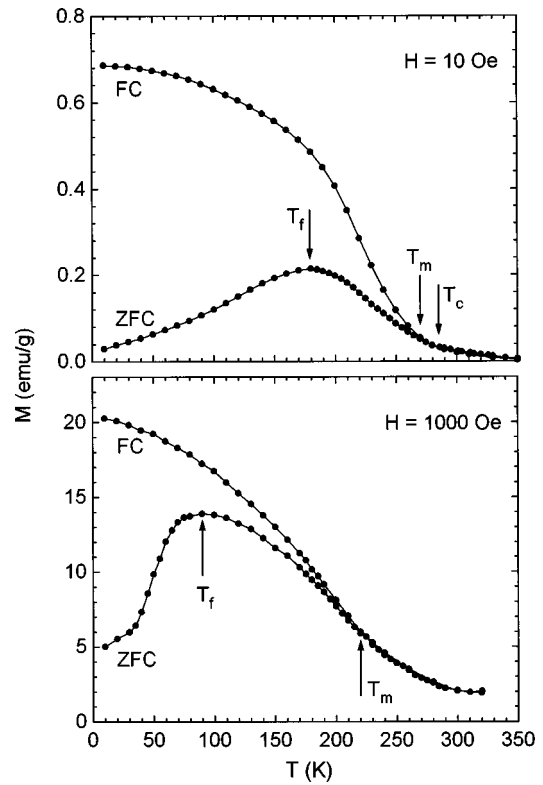

FIG. 2. ZFC and FC magnetizations as functions of temperature at different magnetic fields. T_f is the defreezing temperature of CG state, T_m is the merging temperature for ZFC and FC magnetizations, and T_c is the transition temperature from FM to PM. For the spontaneous magnetic state, at $T<T_f$ the system is in CG state, at $T_f<T<T_m$ it is in CG and FM mixed states, and at $T_m<T<T_c$ it is in a FM state. The lines are guides for eyes.

temperature T_f, then decreases with increasing temperature. The ZFC and FC magnetization characteristics suggest that the spontaneous magnetic state at low temperature is a magnetic CG-like state, and a low external magnetic field, such as 10 Oe, can induce a long range FM order in the system, and thus the crossover from CG to FM occurs. The maximum position T_f of M_{ZFC} marks the defreezing of CG, above T_f the system gradually approaches to FM state. The differ-
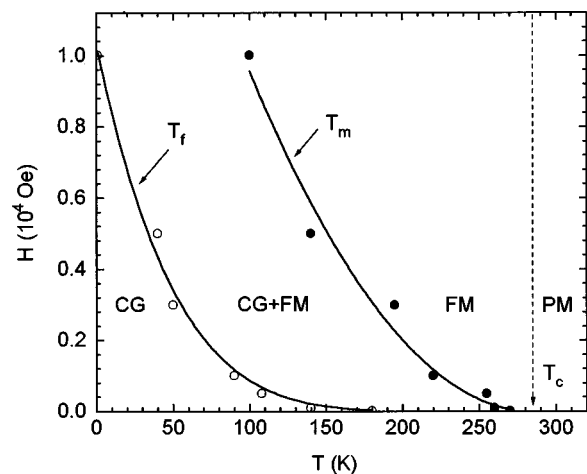

FIG. 3. Magnetic field dependence of the defreezing temperature T_f and merging temperature T_m. The dots are the experimental data and the solid lines are the fits based on Eq. (1).

FIG. 5. Schematic illustration of a double-well model for magnetization relaxation.
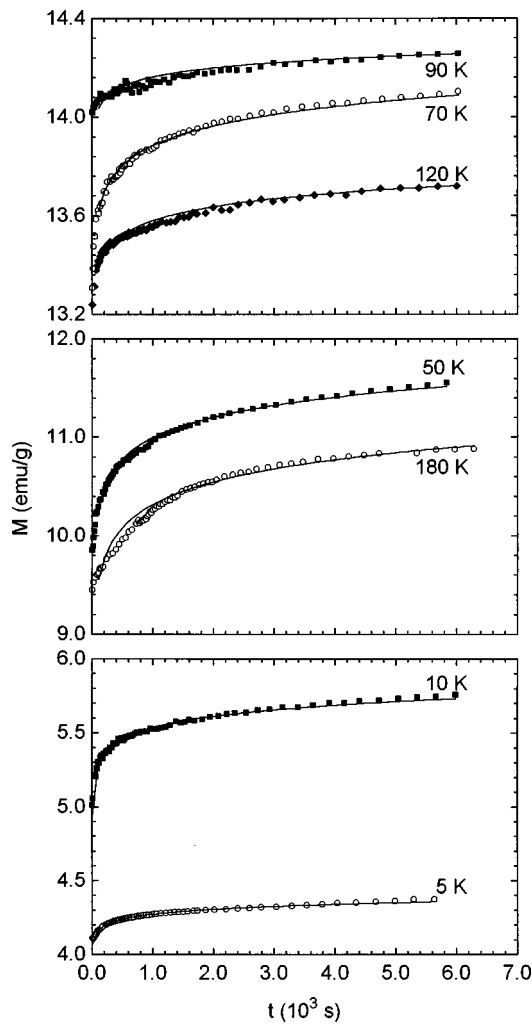
FIG. 4. Magnetization relaxation at different temperatures in a field of 1000 Oe. The dots are the experimental data and the solid lines are the calculated results in terms of Eq. (4) with the parameters listed in Table I. The relaxation data in the field were collected after the sample had been cooled in zero magnetic field from above T_c to 5, 10, 50, 70, 90, 120, and 180 K, respectively.

ence between $M_{ZFC}(T)$ and $M_{FC}(T)$ persists up to 270 K in 10 Oe and up to 220 K in 1000 Oe. The merging point T_m for $M_{ZFC}(T)$ and $M_{FC}(T)$ implies that the system is in the same FM state for ZFC and FC processes above that temperature.

Figure 3 shows the magnetic phase diagram obtained from the ZFC and FC magnetization measurements. At low temperature and low field, the system is in a CG state. At higher temperatures it is in a mixed state of CG and FM. If the external field or temperature is high enough, the system is in FM state. T_f and T_m decrease with increasing H due to the cluster reorientation induced by magnetic field, and the relationships of T_f and T_m with H are given by

$$H_j = H_{0j}(1 - T_j/T_c)^{n_j}, \quad j = f, m, \quad (1)$$

where $H_{0f} = 1.03 \times 10^4$ Oe, $n_f = 5.8$ for the defreezing of CG, and $H_{0m} = 2.19 \times 10^4$ Oe and $n_m = 2.0$ for the merging of ZFC and FC curves for $La_{0.7}Sr_{0.3}Mn_{0.7}Co_{0.3}O_3$.

The broadened coexistence region of CG and FM implies that it is not easy to rearrange all the clusters to form a

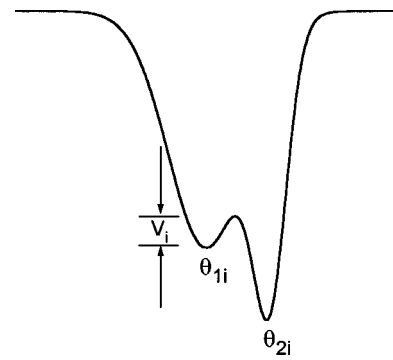well-ordered FM state along the external magnetic field below T_m for ZFC process. In other words, the FM interaction Mn^{4+}–O–Mn^{3+} is weakened due to Co doping, and the system will be semiconductor-like as a result. The reason can be regarded as due to the following two aspects:[6] (i) Co^{3+} is often found to be in a diamagnetic low spin state with a configuration $t_{2g}^6 e_g^0$ at room temperature and below, and (ii) the amount of Mn^{4+} in the system decreases as Co is substituted for Mn. Thus, the doping of Co tends to break down the long range FM order.

The difference in the ZFC and FC magnetizations indicate that the magnetic phase can change from CG to FM. In the following experiments one can see that the CG state can also gradually relax to a FM phase under a magnetic field.

Figure 4 shows the time dependencies of the magnetizations for $La_{0.7}Sr_{0.3}Mn_{0.7}Co_{0.3}O_3$. The increase of magnetization with time means that the clusters would gradually reorient to a more stable state in the direction of an external magnetic field. This rearranging process can be illustrated in terms of a phenomenological double-well model as shown in Fig. 5. The spontaneous magnetic state of cluster i is in such a state with a potential well V_i in the direction of θ_{1i} which is the angle between a fixed axis and the intrinsic magnetic moment μ_i of cluster i. The interaction between the magnetic moment and the magnetic field results in the cluster reorients to a more stable state indicated by θ_{2i}. The probability for cluster i to rearrange from θ_{1i} to θ_{2i} is given by the Boltzmann's Law and is proportional to $e^{-(V_i - \epsilon_i)/k_B T}$, where ϵ_i is the driving energy caused by the applied field, and k_B is the Boltzmann's constant. According to the relaxation theory of physical properties,[19,20] one can assume further that ϵ_i follows the equation $\epsilon_i = \epsilon_{0i} - k_B T \ln(A_i t)$, where the frequency factor A_i is a constant, and ϵ_{0i} is related to the magnetic field and temperature. Using the first-order kinetic equation for relaxation, the probability P_i that the cluster is oriented in $\theta_i = \theta_{1i}$ is:

$$\frac{dP_i}{dt} = \frac{P_i - 1}{\tau_i}, \quad (2)$$

where the proportionality factor τ_i is in the form $\tau_i = \tau_{i0} \exp[(V_i - \epsilon_i)/k_B T]$, and τ_{0i} is a pre-exponential factor. Thus, the contribution of cluster i to the magnetization is

$$M_i = \mu_i P_i \cos \theta_{1i} + \mu_i (1 - P_i) \cos \theta_{2i}. \quad (3)$$

TABLE I. Parameters used to fit the magnetization data to Eq. (4).

T	α (emu/g)	β (emu/g)	$\gamma \times 10^{-2}$
5K	20.33	16.38	0.303
10K	20.24	15.49	0.754
50K	19.21	10.36	3.333
70K	18.27	5.26	2.635
90K	17.21	3.33	1.247
120K	15.24	2.24	4.152
180K	11.52	3.64	13.3

For simplicity, one can assume that $V_i = V$, $\epsilon_{i0} = \epsilon_0$, $A_i = A$ and $\tau_{0i} = \tau_0$ for all clusters. Considering the total contribution of all the clusters and combining Eqs. (2) and (3), the magnetization of the system is given by

$$M = \sum_i M_i = \alpha - \beta(t/t_0)^\gamma. \qquad (4)$$

Here $\alpha - \beta = \Sigma_i M_{0i} = \Sigma_i \mu_i \cos\theta_{1i}$ is the initial magnetization, $\alpha = \Sigma_i \mu_i \cos\theta_{2i}$ is the equilibrium value of magnetization, and $\gamma = (\tau_0 A)^{-1} e^{-(V-\epsilon_0)/k_B T}$. As can be seen in Fig. 4, Eq. (4) fits our experimental data well using the parameters listed in Table I. This implies that the phenomenological double-well model is consistent with the experimental data.

From the above calculation, one can see that the spontaneous magnetization, $\alpha - \beta$, and the equilibrium value, α, of Eq. (4) coincide with the experimental data of the ZFC and FC magnetizations, respectively, as shown in Fig. 6. The lines in Fig. 6 represent the ZFC and FC experimental data and the dots are the calculated results using Eq. (4). The significance of the present set of experiments is that it reveals that the metastable CG-like state can relax to the FM state in a magnetic field.
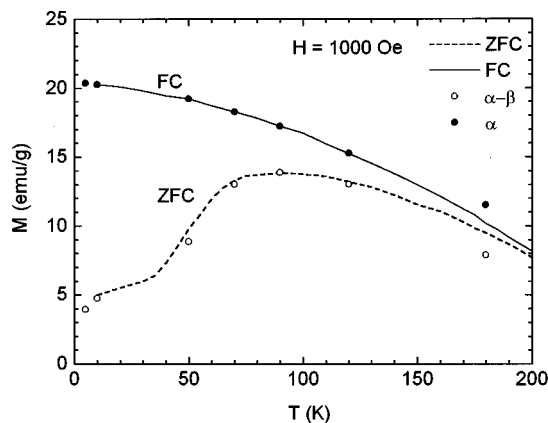

FIG. 6. Comparison of the calculated results (dots) of $\alpha - \beta$ and α and the experimental data (lines) of ZFC and FC magnetizations $H = 1000$ Oe).

As can be seen from Eq. (4), if the parameter γ is very small, the equation can be expanded into the Taylor series to the lowest order of γ as $M = \alpha - \beta + \beta\gamma \ln(t/t_0)$. In this case, we get a logarithmic time dependence of magnetization relaxation. Analogous behavior was found in $La_{2/3}Ca_{1/3}MnO_3$ thin films for which the resistance shows a logarithm time dependence approximately below T_c.[21]

IV. CONCLUSION

In summary, the spontaneous magnetization of $La_{0.7}Sr_{0.3}Mn_{0.7}Co_{0.3}O_3$ polycrystal at low temperatures is in a metastable CG state, but a low field of 10 Oe can induce a long-range magnetic order in the system. The weakness of the double-exchange interaction of $Mn^{4+}-O-Mn^{3+}$ due to Co doping broadens the coexistence region of the CG and FM states. The spontaneous CG state can cross over to the FM state through a relaxation which follows a power law.

ACKNOWLEDGMENTS

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