Evolution of Griffiths phase and spin reorientation in perovskite manganites

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ABSTRACT

Magnetic properties of polycrystalline La$_{1-x}$Ca$_x$Mn$_3$O$_7$Cu$_{1-x}$O$_3$ (0.02 ≤ x ≤ 0.4) have been investigated in detail. All samples show a clear ferromagnetic-paramagnetic transition. The Curie temperature $T_C$ decreases with increasing Ca-dopant. Inverse susceptibility of all the samples deviates from Curie-Weiss law above $T_C$, indicating the presence of a short range ferromagnetic and/or antiferromagnetic ordering state in the paramagnetic background. For 0.02 ≤ x ≤ 0.2, the upward deviation is attributed to antiferromagnetic interactions, while the downward for x ≥ 0.3 is caused by a Griffiths-like behavior, which is suppressed by an applied field. A charge ordering transition associated with an antiferromagnetic phase is detected in x ≥ 0.3 samples, the melting of which results in a spin reorientation transition and a new FM phase. Finally, the phase diagrams of this manganite system have been established.

1. Introduction

Perovskite manganese oxide, which possess the general chemical formula $R_{1-x}A_x$Mn$_3$O$_7$ (R and A means rare- and alkaline-earth metal elements, respectively) have attracted much attention and been extensively studied because of their rich physical content and wide potential industrial applications, such as colossal magnetoresistance (CMR) etc. Previous works reported that the matrix LaMnO$_3$ is an A-type antiferromagnetic insulator below its Neel temperature $T_N$ = 251 K [6]. Above $T_C$, the paramagnetic (PM) behavior in manganites can be described by a Curie-Weiss (C-W) law. For 0.5 < x < 0.9, La$_{1-x}$Ca$_x$Mn$_3$O$_7$ is of a CO-AFM state [7,8].

In recent studies, the observation of Griffiths phase (GP) in doped perovskite manganites, which means the presence of nanoscale magnetic inhomogeneity in the nominal PM region, has been widely reported [9,10]. Different from conventional PM state, GP is a peculiar magnetic state with nonlinear inverse magnetic susceptibility above $T_C$, in which finite size magnetic clusters exist [11]. According to early Griffiths’ prediction [12], GP probably arises in a randomly diluted Ising FM system, in which the magnetization cannot be analyzed by temperature and magnetic field. In 1987, Griffiths’ theory was extended to a bond distribution which can reduce transition temperature, and the anomaly of thermal-magnetic data deviating from C-W law over the temperature range $T_C < T < T_G$ was referred to as a typical characteristic of GP [13]. Here, the Griffiths temperature $T_G$ determines the upper limit for the appearance of GP. It is common that GP is influenced by the grain size and surface effects [10,14,15]. However, the microscopic physical phase diagram and phase separation mechanism of GP behavior accompanying compositional doping in strongly correlated perovskites are still not clear.

More recently, many studies on the substitution of Mn in manganites were made with other transition metal elements to explain the correlation between compositions and basic physical properties [16-19]. In consideration of the fascinating role of Cu in perovskite high temperature superconductor, we prepared and studied the electrical and magnetic behaviors below $T_C$ in LaMn$_{1-x}$Cu$_x$O$_3$ and...
La_{0.7}Ca_{0.3}Mn_{0.9}Cu_{0.1}O_3 perovskites [20,21]. In this work, an unexpected Griffiths-like behavior and spin reorientation transition were observed in polycrystalline La_{1-x}Ca_xMn_{0.9}Cu_{0.1}O_3 system. We studied the evolution of GP under various temperatures and magnetic fields and proposed that the spin reorientation transition is caused by the melting of a CO-AFM state. Finally, the phase diagrams of this perovskite system were achieved.

2. Experimental

Polycrystalline samples of La_{1-x}Ca_xMn_{0.9}Cu_{0.1}O_3 (LCMCO, x = 0.02, 0.05, 0.1, 0.2, 0.3, 0.4) were synthesized by a standard solid-state reaction method. A detailed description of the technique was published elsewhere [21]. The structural characterization was carried out with X-ray powder diffraction (XRD, Rigaku 18 kW D/max-2500 diffractometer with Cu-Kα radiation) at room temperature. As shown in Fig. 1, the XRD patterns indicate that all the samples are in the perovskite structure (space group R3m) with no mixed phases. Magnetic measurements were all performed by employing a physical property measurement system (PPMS-9, Quantum Design Inc., USA) on a vibrating sample magnetometer (VSM option on PPMS-9).

3. Results and discussion

The temperature dependence of magnetization recorded during zero-field-cooling (ZFC) and field-cooling (FC) processes at a magnetic field of 50 Oe for LCMCO system is plotted in Fig. 2. All samples show an obvious FM-PM transition. The transition temperature T_C turns to be lower with the increasing Ca doping (x). Compared with the optimal doping content x = 0.33 in La_{1.0}Ca_{0.3}MnO_3 system, the present x = 0.2 sample shows a maximum of saturation magnetization, which has an optimal Mn^{3+}/Mn^{4+} ratio of 2:1 with Ca^{2+} and Cu^{2+} co-doping. That is, the introduction of both Ca^{2+} and Cu^{2+} converts part of Mn^{4+} into Mn^{3+}. For x > 0.2 samples, the magnetization gradually decreases because the Mn^{3+}/Mn^{4+} ratio deviates from 2:1. The phenomenon of the deviation between FC and ZFC magnetization curves is usually ascribed to the appearance of the spin glass or cluster glass state which arises due to magnetic anisotropy [14]. As listed in Table 1, the effective magnetic moment \( \mu_{\text{eff}} \) which can be deduced from the experiment data (\( g_{\text{FB}} = 2.82/\sqrt{C} \), where C is the fitting parameters of the C-W law), is a little larger than the theoretical prediction (\( g_{\text{FB}} = g_{\text{FF}} \sqrt{S(S + 1)} \)), where g = 2 is the Lande factor, and S = 2 for Mn^{3+}. This is probably due to small magnetic polarons existing in diluted magnetic semiconductors [22]. It is reported that the short-range interacting FM clusters above \( T_C \) nucleated in GP may be prerequisites of the glassy phase at low temperatures [23]. That is, there might be a Griffiths-like phase in present system.

Fig. 3 presents the inverse ZFC dc susceptibility (\( \chi^{-1} = H/M \)) data of LCMCO samples. The green line is the best fit of C-W law in PM region. It is interesting that \( \chi^{-1}(T) \) curve deviates from the linear fitting from a temperature above \( T_C \). For x = 0.2 samples, the observed upward deviation in the inverse susceptibility from C-W law means that \( \chi(T) \) is lower than the values expected for a pure PM phase. Zhou et al. [24] proposed that the AFM correlation among the neighboring short-range FM clusters accounts for the observed upward deviation. The Griess temperature \( T_C \) is defined as the onset temperature, where \( \chi^{-1}(T) \) data deviates from C-W law, and a local AFM ordered area begins to develop [25]. For x = 0.3 and 0.4 samples, the inverse susceptibility shows a downturn deviation from C-W law. This is a determining characteristic feature of GP, which meets the power law:

\[
\chi^{-1}(T) \propto (T - T_{C,\text{Rand}})^{1-\lambda} (0 \leq \lambda < 1)
\]

Power law is a generalized C-W law. The exponent \( \lambda \) shows the strength of GP and the value of \( T_{C,\text{Rand}} \) can be obtained from \( \lambda = 0 \) in the C-W regime [26], which is equivalent to Curie-Weiss temperature (\( \theta_p \)). The double logarithmic plots of inverse susceptibility against temperature \( T_{\text{inv}} = T/T_{C,\text{Rand}} - 1 \), reproduced in the insets of figures, show a linear behavior at low \( T_{\text{inv}} \) and confirm the proposed GP. The obtained related parameters are listed in Table 1. The value of \( \lambda \) for

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**Fig. 1.** Room temperature X-ray diffraction patterns of La_{1-x}Ca_xMn_{0.9}Cu_{0.1}O_3 system.

La_{0.7}Ca_{0.3}Mn_{0.9}Cu_{0.1}O_3 perovskites [20,21].

**Fig. 2.** Temperature dependence of the zero-field-cooling (ZFC) and field-cooling (FC) dc magnetization under H = 50 Oe for La_{1-x}Ca_xMn_{0.9}Cu_{0.1}O_3 system.

**Table 1.** Parameters obtained from Figs. 2 and 3 for La_{1-x}Ca_xMn_{0.9}Cu_{0.1}O_3 system under H = 50 Oe. \( T_C, T_{C,\text{Rand}}, \mu_{\text{eff}}, \chi_p \) is Curie temperature, random transition temperature, effective magnetic moment and random transition temperature, respectively. Curie-Weiss temperature \( \theta_p \) is equivalent to \( T_{C,\text{Rand}} \). The Griffiths temperature \( T_C \) determines the upper limit for Griffiths phase (GP). The exponent \( \lambda \) shows the strength of GP in column GP, Y means GP exists, N means GP cannot be observed.

<table>
<thead>
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<th>x</th>
<th>( T_C ) (K)</th>
<th>( T_{C,\text{Rand}}/\theta_p ) (K)</th>
<th>( \mu_{\text{eff}} ) (( \mu_B ))</th>
<th>( T_C ) (K)</th>
<th>( \lambda )</th>
<th>( T_{CO} ) (K)</th>
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</tr>
<tr>
<td>0.1</td>
<td>152.73</td>
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<td>6.09</td>
<td>--</td>
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<td>--</td>
<td>--</td>
<td>--</td>
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<tr>
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$x = 0.3$ is a little larger than $x = 0.4$, implying a depressed tendency of GP with increasing Ca dopant. The slope changes as marked by blue arrows at 158.12 K and 144.64 K for $x = 0.3$ and 0.4 respectively, are attributed to the presence of a CO state [28,29].

To further investigate the evolution of GP and CO state under an applied field, a systematic measurement of magnetization under various magnetic fields has been carried out. Fig. 4 shows the temperature dependence of ZFC magnetization under a dc field increased from (a) 50 Oe to (b) 30 kOe. The derivation $dM/dT$ vs $T$ curves are also plotted to the right axis to define the phase transition characteristics. Associated with the three distinct anomalies in $dM/dT$ curves, three phase transitions are recognized. The sharp peak at $T_C$ as indicated by red arrows in $dM/dT$ curves corresponds to the large variation of $M(T)$ data and declares the establishment of FM double-exchange interaction. As listed in Table 2, $T_C$ rises with an increasing applied field. The visible step-like change of $M$ at $T_N$ in both FC and ZFC curves for $x = 0.3$ suggests an AFM transition of Mn$^{3+}$ spin components. Here, $T_N$ is identified as the peak temperature in $dM/dT$ curves. Similar behaviors have been observed in Pr$_{3/8}$Ca$_{3/8}$MnO$_3$ manganites [29]. The sample is in a phase coexistence state of antiferromagnetism and ferromagnetism at a temperature lower than $T_N$. The transition from AFM to FM state can be achieved by increasing temperature and magnetic field, which will promote the growth of the FM fraction and result in a step-like change of $M$. In Fig. 4(h), the step-like change of $M$ at $T_N$ is nearly undetectable at $H = 30$ kOe, indicating a nearly pure FM state below $T_C$. Just above $T_C$, an inconspicuous slope change of the $M(T)$ curve is usually ascribed to a CO transition in doped manganites [28]. The CO transition temperature $T_{CO}$, at which the obvious kink in the derivative $dM/dT$ curves in Fig. 4(a)–(e) is observed, is marked by blue arrows and listed in Table 2. The magnetization change ratio, $dM/M$, keeps decreasing from 50 to 500 Oe and increasing from 500 to 20 kOe, illustrating the evolution of phase separation below $T_N$. $T_{CO}$ remains nearly unchanged under various magnetic fields. In Fig. 4(h), the transition at $T_N$ can hardly be observed in $M(T)$ curve, illustrating the weak AFM transition at a high magnetic field $H = 30$ kOe. $T_{CO}$ is overwhelmed by the rising $T_C$ and the overlapped FM transition. Interestingly, a new sharp peak rather than a small hump in $dM/dT$ curves is observed at $T_{SR}$ for a higher applied field $H \geq 10$ kOe in Fig. 4(f)–(h), indicating a second FM transition. It is well known that the spin components of Mn$^{3+}$ of LaMnO$_3$ are coupled parallel to each other in the ab plane, and they are antiparallel along c-axis. In La$_{0.7}$Ca$_{0.3}$MnO$_3$ manganite, all the spin components of Mn$^{3+}$ and Mn$^{4+}$ are coupled because of a Mn$^{3+}$–O–Mn$^{4+}$ double-exchange mechanism [5]. In the studied LCMCO system, Cu$^{2+}$ partially replaces Mn$^{3+}$ and causes disorder in the system, which may be the origination of CO-AFM phase and GP. The spin reorientation transition at $T_{SR}$ may originate from the melting of the CO phase, which results in a generation of the FM content [29]. Therefore, there coexist two different FM phases at low temperatures, and the second FM phase can be controlled by an external magnetic field.

Inverse susceptibility versus temperature curves for LCMCO ($x = 0.30$) under various magnetic fields are plotted as Fig. 5. $T_{CO}$ can also be recognized as an apparent hump, as indicated by blue arrows. As reported in previous study [24], the CO transition usually induces simultaneously an AFM ordering phase and makes the inverse susceptibility plotted curves upward. In Fig. 5 (a)–(e), $H < 10$ kOe, a downturn of $\chi^{-1}(T)$ curves at $T_{CO}$ proofs the existence of a short-range ordering GP. The linear fitting of the power law (formula (1)) in the insets helps to give the exponent $\lambda$. As shown in Table 2, $\lambda$ decreases with increasing magnetic field, indicating the field suppression effect to GP due to the polarization of spins outside the clusters [30]. In Fig. 5(f)–(h), $H \geq 10$ kOe, the downturn behavior cannot be observed.
The physical phase diagrams for the present system are finally plotted as Figs. 6 and 7. One can see a PM phase at high temperatures for all samples. In Fig. 6, a Griffiths phase and CO-AFM phase are generated above $T_c$ in $x = 0.3$ and 0.4 samples. $T_c$ decreases gradually as Ca content $x$ increasing. For $x = 0.3$ and 0.4 samples, the Mn$^{3+}$/Mn$^{4+}$ ratio approaches to 1:1, which leads to the presence of a CO transition. Furthermore, the pivotal Mn$^{3+}$-O-Mn$^{4+}$ chains are partly cut off by the B-site Cu$^{2+}$ ions, which prevents the transport of $e_g$ electrons by double-exchange interaction. Area between $T_{CO}$ and $T_{SR}$ was referred to as a GP, which involves short-range FM clusters in PM region. The $T$-$H$ phase diagram for LCMCO ($x = 0.30$) sample in Fig. 7 shows that, at a low magnetic field $H < 10$ kOe, the regions depicted from low to high temperature are FM phase, CO phase, GP and PM phase. $T_{CO}$ and $T_0$ remain nearly unchanged under various magnetic fields, while $T_c$ increases with the magnetic field. At a high enough field, $\lambda = 0$ and $T_c = T_G$, as shown by the dash line. At fields $H \geq 10$ kOe, the CO phase melts and converts into another FM phase. A new spin reorientation transition confirms the conjecture.

4. Conclusion

In summary, we have investigated magnetic behavior of polycrystalline LCMCO system. All samples show a clear FM-PM transition and $T_c$ turns to be lower with the increasing $x$. The departure of ZFC curve from FC curve indicates complex interactions below $T_c$. Derivation of PM magnetization data from C-W law indicates the presence of a short-range FM and/or AFM ordering state. The downward derivation suggests that the GP model is appropriate to describe the
short-range ordered state, while the upward deviation is caused by AFM interactions. The experimental data show that the GP is suppressed by an increasing magnetic field. There is a CO transition in $x = 0.3$ and $0.4$ samples. The spin reorientation transition observed at $H \geq 10$ kOe for $x = 0.3$ sample is due to the melting of the CO state, which results in the generation of a second FM phase.

Declaration of Competing Interest

There is no conflict of interest.

Acknowledgments

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<th>$T_m$ (K)</th>
<th>$T_{GO}$ (K)</th>
<th>$T_C$ (K)</th>
<th>$T_{SR}$ (K)</th>
<th>$\theta_p$ (K)</th>
<th>$\lambda$</th>
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Table 2

Parameters obtained from Figs. 4 and 5 for La$_{0.7}$Ca$_{0.3}$Mn$_{0.9}$Cu$_{0.1}$O$_3$ under various magnetic fields. $T_C$, $T_{GO}$, $T_C^{SR}$, $\theta_p$ and $\lambda$ represent the same meaning with parameters in Table 1. $T_{SR}$ is an abbreviation for spin reorientation transition temperature. In column GP, Y means GP exists, N means GP cannot be observed.

Fig. 5. Temperature dependence of inverse ZFC dc susceptibility under various magnetic fields for La$_{0.7}$Ca$_{0.3}$Mn$_{0.9}$Cu$_{0.1}$O$_3$ sample. The straight green lines represent the Curie-Weiss law. The insets are double logarithmic plots according to power law (Eq. (1)), where the solid red lines are the linear fittings at low $T_m$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
no. 02.A03.21.0006).

References