Observation of a Griffiths-like phase in bilayered manganites

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The authors report the observation of a Griffiths-like phase in La$_{2-x}$Sr$_{1+x}$Mn$_2$O$_7$ (x = 0.30, 0.33, and 0.40) and (La$_{0.8}$Eu$_{0.2}$)$_{2-x}$Sr$_{1+x}$Mn$_2$O$_7$ (x = 0.33) single crystals by means of electron spin resonance, magnetic susceptibility, and magnetoresistance measurements. In the temperature region $T_C < T < 350$ K, the resonance signal consists of a ferromagnetic resonance line and a paramagnetic resonance line, which suggests that the system is not in a pure paramagnetic phase. The ferromagnetic resonance signal disappears and the magnetic susceptibility starts to deviate from the Curie-Weiss law at the same temperature $T^* = 350$ K, independent of doping level and anisotropy. These results indicate that a Griffiths-like phase exists at $T_C < T < T^*$ in bilayered manganites, which is due to intrinsic inhomogeneity caused by quenched disorder. © 2007 American Institute of Physics. [DOI: 10.1063/1.2431061]

Perovskite manganites have attracted considerable attention since the discovery of the colossal magnetoresistance (CMR) effect. Recently, some significant works have confirmed that quenched disorder can induce nanoscale intrinsic inhomogeneities in manganites above the magnetic ordering temperature $T_C$, which is important to understand CMR effect in paramagnetic region. Dagotto et al. have proposed a scale $T^*$ above $T_C$ as a temperature of cluster formation in manganites with quenched disorder, which is the analog of the Griffiths temperature in cuprates. At $T_C < T < T^*$, there exists short-range ordering ferromagnetic (FM) clusters in a paramagnetic (PM) matrix. Since the FM clusters can be metallic, percolation may be induced by connecting part of the FM clusters when temperature decreases or magnetic field increases. Tiny changes in the metallic fraction can induce large change of conductivity in this percolative region, which correlates with CMR effect. But, the correlation of a Griffiths-like phase and CMR effect needs to be confirmed further. Now, analyzing the Griffiths-like phase in detail and searching for a characterization of $T^*$ should be pursued actively in experiments.

At present the study of a Griffiths-like phase in manganites mainly focuses on the cubic ABO$_3$ system. Recently, Deisenhofer et al. have reported the discovery of a triangular phase regime in the phase diagram of La$_{1-x}$Sr$_x$MnO$_3$ manganites above $T_C$ using electron spin resonance (ESR) and magnetic susceptibility measurements. In this phase regime, FM entities coexist with the globally PM phase. The authors think that the nature of this phase is due to the presence of correlated quenched disorder in the orthorhombic phase. In bilayered manganites La$_{2-x}$Sr$_{1+x}$Mn$_2$O$_7$, the existence of CMR and colossal electroresistance (electric-field-induced resistance change), both related with phase separation, has been reported. But the detailed study of Griffiths-like phase in this system has not yet been performed. Due to strong anisotropy and dimensional effect in bilayered manganites, a systemic analysis of a Griffiths-like phase and its dependence on anisotropy and dimensionality requires a complete ESR mapping on high-quality single crystal samples. Burgy et al. have suggested that the tolerance factor may not substantially affect the Griffiths temperature $T^*$, although it changes the ordering temperature significantly. The dependence of Griffiths temperature $T^*$ on doping and tolerance factors in bilayered manganites should also be clarified.

In this work, we have performed ESR, magnetic susceptibility, and resistivity measurements on a series of La$_{2-x}$Sr$_{1+x}$Mn$_2$O$_7$ (x = 0.30, 0.33, and 0.40) single crystals. We find a transition temperature of $\sim 350$ K which corresponds to the Griffiths temperature, independent of doping level and anisotropy. In addition, the ESR data on a Eu-doped (La$_{0.8}$Eu$_{0.2}$)$_{2-x}$Sr$_{1+x}$Mn$_2$O$_7$ (x = 0.33) single crystal give the same Griffiths temperature of 350 K, which supports the theory of Burgy et al.

Single crystals of La$_{2-x}$Sr$_{1+x}$Mn$_2$O$_7$ (x = 0.30, 0.33, and 0.40) and (La$_{0.8}$Eu$_{0.2}$)$_{2-x}$Sr$_{1+x}$Mn$_2$O$_7$ (x = 0.33) were grown by the floating-zone method in an optical image four-mirror furnace. X-ray diffraction measurement on powders shows no trace of any secondary phase. The composition of the crystals is checked by inductively coupled plasma atomic emission spectroscopy. Backreflection Laue x-ray diffraction method was carried out to determine the crystallographic direction. The magnetic properties were measured using a superconducting quantum interference device magnetometer (Quantum Design, MPMS-7). Transport measurements were performed using the standard four-probe method. The ESR measurements at 9.5 GHz (X band) were taken in a JEOL ESR spectrometer.

Figure 1 shows the in-plane ESR spectra of La$_{2-x}$Sr$_{1+x}$Mn$_2$O$_7$ (x = 0.33) at several selected temperatures in paramagnetic regime from 120 to 364 K. Above Curie temperature $T_C \sim 120$ K, the spectrum consists of a paramagnetic resonance (PMR) line centered at 3.2 kOe (g value is close to 2) and a ferromagnetic resonance (FMR) line at lower resonance field, which suggests that the system is not in a pure paramagnetic phase above $T_C$. When temperature changes from 120 to 460 K, the PMR field almost remains stationary in every spectrum. By analogy with La$_{1-x}$Sr$_x$MnO$_3$ oxides, these PMR signals should be mainly due to the...
contribution of Mn$^{3+}$ and Mn$^{4+}$ spins. Due to the increase of the local magnetic fields of the crystal, FMR signal shifts to lower resonance fields as temperature decreases. The intensities of PMR and FMR are used to identify the nature of the magnetic ions contributing to the resonance which can be proportional to the number of spins. Here, we use the double integration of the observed ESR spectrum to calculate the number of spins. Here, we use the double integration of the observed ESR spectrum to calculate the number of spins.

In Fig. 2(a), we show temperature dependence of the FM and PM resonance fields in the La$_{2−2}$Sr$_{1+2}$Mn$_2$O$_7$ (x = 0.33) crystal. Above the Curie temperature 120 K, the PMR signal begins to appear and the FMR line gradually approaches to the PMR line with increasing temperature. At ~350 K, all lines merge into a single PMR line regardless of ab plane or c direction. This temperature (350 K), at which the FM clusters disappear completely, can be defined as a Griffiths temperature $T^*$. In the temperature range $T_{C}<T<T^*$, the system is in a Griffiths-like phase in which ferromagnetic clusters coexist with paramagnetic matrix. This argument is further supported by magnetic susceptibility measurements. As shown in Fig. 2(b), between $T_{C}$ and $T^*$, the inverse magnetic susceptibility exhibits a nonlinear dependence with temperature and does not obey the Curie-Weiss law. The observed temperature $T^* ~ 350$ K at which the magnetic susceptibility starts to deviate from the Curie-Weiss law is consistent with that drawn from the ESR data.

To correlate the Griffiths-like phase and CMR effect, we also measured temperature dependence of in-plane resistivity and magnetoresistance (MR) in La$_{2−2}$Sr$_{1+2}$Mn$_2$O$_7$ (x = 0.33). As shown in Fig. 3 a CMR effect is observed around the metal-insulator transition. The MR ratio decreases with increasing temperature and goes to zero at 350 K, as shown in the inset of Fig. 3(b). We note that this temperature is just the Griffiths temperature. Therefore, it suggests that the MR effect above $T_C$ is closely related to the Griffiths-like phase.

To further confirm a Griffiths-like phase in bilayered manganites and investigate the effect of doping level and tolerance factor, we also measured ESR spectra of La$_{2−2}$Sr$_{1+2}$Mn$_2$O$_7$ (x = 0.30 and 0.40) and (La$_{0.8}$Eu$_{0.2}$)$_{2−2}$Sr$_{1+2}$Mn$_2$O$_7$ (x = 0.33) crystals. For each sample, a FMR line in addition to a PMR line appears in the paramagnetic state for a broad temperature range. Figure 4 shows temperature dependence of the resonance fields of the FM and PM signals above $T_C$. All crystals exhibit a similar
Griffiths-like temperature $T^* \sim 350$ K along both crystalline directions, although they have quite different magnetic ordering temperature. These results indicate that this temperature scale is almost independent of doping and dimensional effect.

The onset of a Griffiths-like phase in bilayered manganites can be understood in terms of the intrinsic inhomogeneity induced by quenched disorder. Because of the strong coupling of Jahn-Teller distortion of the $\text{Mn}^{3+}$ ions and crystal lattice, the disorder in La$_{2-x}$Sr$_{x+2}$Mn$_2$O$_7$ is quenched within the distorted structure and the FM bonds can be fixed within the anomaly lattice. Thus, the FM clusters can be nucleated and stabilized by this correlated interactions. In addition, the chemical disorder due to random distribution of La$^{3+}$ and Sr$^{2+}$ ions on A site leads to local Sr enrichment or poorness, which results in the local FM interactions and antiferromagnetic (AFM) coupling in the system. The theory of Burgy et al.\(^7\) has testified that the competition of FM and AFM phases can stabilize and enhance the Griffiths phase. Therefore, correlated disorder and the two-phase competition in the system should be mainly responsible for the stabilization and enhancement of the Griffiths-like phase. These ideas have been considered by Deisenhofer et al.\(^{10}\) in La$_{1-x}$Sr$_x$MnO$_3$ system and by Magen et al.\(^{15}\) in magnetocaloric compound Tb$_5$Si$_2$Ge$_2$, in which a Griffiths-like phase has been observed.

In conclusion, the ESR spectra of a series of La$_{2-x}$Sr$_{x+2}$Mn$_2$O$_7$ ($x=0.30$, 0.33, and 0.40) and (La$_{0.8}$Eu$_{0.2}$)$_{2-x}$Sr$_{x+2}$Mn$_2$O$_7$ ($x=0.33$) support the onset of a Griffiths-like phase in bilayered manganites. The Griffiths temperature is found to be insensitive to the hole doping level, the tolerance factor, and anisotropy. Moreover, the MR ratio goes to zero just at the Griffiths temperature, which suggests a close correlation between the Griffiths-like phase and the CMR effect.

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