Electron spin resonance study of spin correlations in charge-ordered La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$(x=0.6)

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Electron spin resonance (ESR) studies have been performed on a bilayered manganite La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$(x=0.6) single crystal. The charge ordering (CO) and antiferromagnetic (AFM) transitions can be well identified from the ESR spectra in both the ab plane and c axis directions. A coexistence of paramagnetic resonance signal and low-field AFM resonance signal was observed below the CO temperature $T_{CO}$. The analysis of the ESR parameters as a function of temperature suggests the existence of weak ferromagnetic (FM) correlations in the paramagnetic state and AFM correlations below $T_{CO}$. The competition of FM and AFM correlations results in a broad peak in ESR intensity. Our results also show that the intensity of AFM correlations increases with decreasing temperature as the system enters from the CO state into the A-type AFM ground state. Therefore, the evolution and anisotropy of spin correlations can be fully mapped by ESR study.


I. INTRODUCTION

The study of charge ordering (CO) in hole-doped ABO$_3$ manganites has attracted considerable attention during the past decades, not only for fundamental physics but also for potential applications. For example, the magnetic field induced melting of charged ordered state may lead to a large magnetoresistance effect as well as a giant magnetocaloric effect. Neutron scattering results on these manganites have proved that ferromagnetic (FM) spin fluctuations exist even in the paramagnetic phase, and they change over to the antiferromagnetic (AFM) spin fluctuations below the onset of CO. The switching of spin fluctuations from FM to AFM at the charge and/or spin ordering temperature typifies the interplay between the orbital charge and spin orderings in doped manganites. However, such spin fluctuations in bilayered manganite La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ have not been studied in detail.

In the La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ system, the bilayered crystal is composed of MnO$_2$ bilayers, which are stacked along the c axis and separated by insulating nonmagnetic (La,Sr)$_2$O$_3$ layers, leading to a quasi-two-dimensional structure. Due to the reduced dimensionality, the electronic and magnetic properties of bilayered manganites are much different from the well-studied ABO$_3$ three-dimensional (3D) manganites. CO behavior was observed in La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ over a broad doping range of 0.47 $\leq x \leq 0.62$. However, unlike the 3D perovskite compounds, the CO state is stable only over a limited temperature range. This suggests that the lower dimensionality directly affects the competition among charge, lattice, and spin degrees of freedom. For example, previous studies on $x=0.6$ showed that the spin correlation is FM within the MnO$_2$ bilayers (i.e., the ab plane) and AFM across the layer (i.e., along the c axis), and it undergoes a CO at $T_{CO} \sim 280$ K and A-type AFM transition at $T_N \sim 150$ K. Between neighboring MnO$_2$ bilayers, there is a weaker FM coupling.

In this work, we have taken the electron spin resonance (ESR) technology to study the magnetic correlations and phase transitions in the charge-ordered La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$(x=0.6). ESR has been proven to be a powerful tool in the study of the magnetic correlation in manganites. Valuable information can be obtained through the study of temperature dependence of ESR spectra and various ESR parameters. Our results indicate that there are weak FM correlations in the paramagnetic state and strong AFM correlations within the MnO$_2$ bilayers (i.e., the ab plane) and across the bilayers (i.e., along the c axis) below CO temperature $T_{CO}$. The ESR studies are thus able to provide valuable information to better understand the CO phenomenon.

II. EXPERIMENTS

The studied single crystal was grown by the floating-zone method in an optical image four-mirror furnace. The composition of the crystal is checked by inductively coupled plasma atomic emission spectroscopy. X-ray diffraction measurement on powder shows no trace of any secondary phase. Back-reflection Laue x-ray diffraction method was carried out to determine the crystallographic direction. A rectangular piece of sample with a of size of $2 \times 1 \times 0.5$ mm$^3$ was cut to take magnetization and ESR measurements. The largest plane is the ab plane. The magnetization was measured using a superconducting quantum interference device magnetometer (Quantum Design, MPMS-7). The ESR experiments were carried out with a JEOL JES-FA200 ESR spectrometer at X-band frequencies ($\nu \approx 9.4$ GHz) in temperature ranging from 100 to 440 K.

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The magnetization is very small for both directions, which coincides with the strong AFM correlations and weak FM correlations in the paramagnetic phase. At high temperature, it follows the Curie–Weiss law and exhibits a positive magnetic susceptibility for both directions. At low temperature, the magnetization shows a sharp peak at 270 K and a wide shoulder at around 150 K in both the ab plane and c axis direction. These two peaks correspond to CO transition temperature $T_{CO}$ and AFM ordering transition $T_N$, respectively. The magnetization is very small for both directions, which coincides with the strong AFM correlations and weak FM correlations in the $x=0.6$ sample. Figure 1(b) shows the inverse magnetic susceptibility for both directions. At high temperature, it follows the Curie–Weiss law and exhibits a linear dependence with temperature. We obtain the Weiss constant $\Theta=30$ K with $H//ab$ and $\Theta=68$ K with $H//c$. The positive values of the Weiss constant reveal the existence of FM correlations between Mn spins above $T_{CO}$. However, the FM correlations are very weak and the FMR signal can hardly be observed in the ESR spectra, which will be discussed below.

Figures 2(a) and 2(b) show the typical ESR spectra recorded with $H//ab$ plane and $H//c$ axis, respectively. The spectra show a weak anisotropy between the $ab$ plane and $c$ axis, which is in contrast to the $x \leq 0.5$ samples where a strong anisotropy was observed. This weak anisotropy should be due to the weaker uniaxial magnetocrystalline anisotropy in this composition. The spectra consist of a broad, nearly isotropic paramagnetic resonance (line A) with g value close to 2. When temperature is below 220 K, a low-field signal (line B) appears for both directions. Through our discussion below, this resonance line should correspond to the AFM resonance line. Below 120 K, the ESR signal is too weak to be recorded for both directions. The spectra are fitted to the Lorentzian line shape function. The line shape parameters, viz., the intensity and the resonance field, are extracted from the fits.

Figure 3 shows the temperature dependence of the ESR intensity including both lines A and B. For both directions, the intensity increases gradually as temperature decreases, showing a broad peak at about 270 K ($-T_{CO}$), and then decreases with further cooling. This behavior is observed in other CO manganites as well and is also consistent with the dc susceptibility data shown in Fig. 1. Neutron scattering on charge-ordered manganites has shown that FM spin fluctuations exist in the paramagnetic phase and are progressively replaced with AFM spin fluctuations as the system goes into the CO state. The broad peak of the intensity near $T_{CO}$ reflects the competition of the FM and AFM correlations as the system enters into the CO state from paramagnetic state, whereas the large decrease in intensity below $T_{CO}$ can be attributed to the development of AFM correlations in the CO state. As temperature further decreases, the ESR intensity shows a weak temperature dependence between $T_N$ and $T_{CO}$ and then decreases rapidly below $T_N$. This behavior was also observed in neutron scattering, which showed that the FM fluctuation decreases rapidly at the onset of the CO. It remains finite for $T_N \leq T \leq T_{CO}$ with little temperature dependence, and then it vanishes completely when the system goes into the entire AFM ground state. Thus, the rapid decrease in intensity below $T_N$ is attributed to the disappearance of FM spin fluctuations on further cooling. Below 110 K, the ESR signal is too weak to be observable. The disappearance of ESR signal at low temperature has been generally observed.
in manganites with AFM ground state. This is due to the fact that the ESR signal intensity is proportional to the magnetization of the sample. Below the AFM transition temperature, the magnetization drops fast, as seen in the $M(T)$ curve in Fig. 1. Thus, the intensity of ESR signal becomes very weak with the formation of long-range AFM correlations.

Figure 4 shows the $g$ factor of the A line for both directions, which is calculated from the resonance field. As temperature decreases from 440 to 200 K across $T_{CO} \approx 270$ K, the $g$ value is close to 2 and shows a weak temperature dependence. It indicates that the FM spin correlations are very weak above 200 K. As temperature decreases close to $T_N$, the $g$ value increases dramatically from 1.93 to 2.24. The prominent increase in $g$ value as temperature decreases from $T_{CO}$ to $T_N$ has been observed in other CO manganites as well. This behavior can be possibly explained by the changes in the spin-orbit coupling constant consequent to the orbital ordering. The neutron scattering results have shown that the orbital ordering of $d_{x^2-r^2}$ and $d_{3z^2-r^2}$ orbitals is accompanied by the CO in bilayered manganites. When temperature decreases from $T_{CO}$ to $T_N$, the orbital ordering builds up and is complete at $T_N$. Therefore, the gradual buildup of the orbital ordering can change the spin-orbit coupling as well as the crystal-field splitting and hence can lead to an increase in the $g$ value as the temperature is lowered.

We discuss below the additional signal (line B) that appears on the lower-field side of the paramagnetic resonance line below 220 K. As temperature decreases from $T_{CO}$ to $T_N$, this signal shifts to the lower field and the intensity is involved with temperature (see Fig. 3). The behavior of line B is similar to the FM resonance signal observed in other manganites. However, through our discussions, we believe this low-field signal should not be the ferromagnetic resonance (FMR) signal but the AFM signal. Generally, the FMR signal should follow the FM resonance mode and shift from low field to high field in the ESR spectra when the applied fields $H$ rotate from the easy plane (i.e., the $ab$ plane) to hard axis (i.e., the $c$ axis). However, in the $x=0.6$ sample, the angular variation in ESR spectra shows no significant change. Additionally, we have done similar ESR experiments on $x=0.55$, where the spectra consist of a paramagnetic resonance signal and a very weak FMR signal. However, a rough estimate obtained by comparing the FMR and PMR signals shows that the fraction of spins contributing to the FMR is $\leq 0.5\%$. In the $x=0.6$ sample, the FM correlation is even weaker than the $x=0.55$ sample. However, in the spectra, the intensity of signal B is close to 10% of signal A at low temperature. This large proportion of spins contributed to signal B cannot be the FM correlation; the low-field B line should be the AFM signal instead of FM signal. In fact when the system is transforming from CO to AFM state, the AFM is in short range ordering, and the coupling of antiparallel spins is weak so that it can be broken by a higher magnetic field leading to the occurrence of AFM resonance signal. However, with the formation of long-range AFM order below $T_N$, it is difficult to observe the AFM signal because of the strong spin coupling that requires a rather large resonance field. This appearance of low-field AFM resonance signal might need further investigations.

The AFM signal appears at about 220 K, lower than the CO transition temperature $T_{CO}$ but higher than the AFM transition $T_N$. It indicates that the AFM correlations are just present below $T_{CO}$ when the system goes from the CO state into AFM ordering state, consistent with the neutron scattering results that proved there are no AFM spin fluctuations above $T_{CO}.^3$ Additionally, some information can be obtained from the intensity of line B. In fact, as temperature further decreases below $T_N$, the magnetization as well as ESR intensity decays dramatically with temperature. It is difficult to obtain the evolution of AFM correlations with temperature from the spectra. However, the relative intensity between the PMR and AFM signals may be used to estimate the development of AFM correlations with temperature. As shown in Fig. 5, the intensity ratio $I_B/I_A$ increases gradually with decreasing temperature, indicating that the AFM correlations increase with decreasing temperature below $T_N$, which is consistent with the neutron scattering results. The inset of this figure shows the intensity for both directions. It increases gradually with the emergence below 220 K and reaches a maximum near 150 K ($\sim T_N$), and then decreases dramatically. This maximum value in the vicinity of $T_N$ is a sign of intrinsic nature of line B. All the results indicate that the AFM correlations increase with the decrease in temperature when the system goes from the CO state into the insulating AFM ground state.
IV. CONCLUSION

We have performed dc magnetization measurements and ESR on a bilayered $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($x = 0.6$) single crystal. A coexistence of paramagnetic resonance signal and low-field AFM resonance signal was observed below the CO temperature $T_{\text{CO}}$. The spectra show very weak anisotropy between the $ab$ plane and $c$ axis. Both the CO and the AFM transitions can be identified from the ESR spectra. The temperature dependence of the ESR spectra and parameters reveals the existence of FM correlations in the paramagnetic state, which are replaced with AFM spin correlations in the CO state. Our results also show that the intensity of AFM correlations increases with decreasing temperature when the system enters into AFM ground state from CO state.

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