An electron spin resonance study of Eu doping effect in $La_{4/3}Sr_{5/3}Mn_2O_7$ single crystal*

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The effect of Eu^{3+} ion doping in the La sites of single-crystal $La_{4/3}Sr_{5/3}Mn_2O_7$ was investigated. Electron spin resonance (ESR) was applied to $La_{4/3}Sr_{5/3}Mn_2O_7$ and $(La_{0.8}Eu_{0.2})_{4/3}Sr_{5/3}Mn_2O_7$ single crystals. A phase separation and phase transitions were observed from the ESR spectra data. Between 350 K and 300 K, both paramagnetic resonance (PMR) and anisotropic ferromagnetic resonance (FMR) lines were observed in the *ab* plane and the *c* axis direction, suggesting a coexistence of the paramagnetic (PM) phase and the ferromagnetic (FM) phase. The magnetization measurement reveals a spin-glass-like behavior in single-crystal $(La_{0.8}Eu_{0.2})_{4/3}Sr_{5/3}Mn_2O_7$ below the temperature of spin freezing T_f ($\sim$ 29.5 K).

Keywords: electron spin resonance, manganite single crystal, phase separation, anisotropy

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1. Introduction

In recent years, perovskite-type manganites have attracted considerable attention for their complex magnetic and transport properties, such as ferromagnetism (FM), intrinsically inhomogeneous ground states (i.e., phase separation), and charge/orbital ordering. A lot of research on this subject has been carried out, both in theoretical and experimental aspects.[1–6] In the $La_{2-2x}Sr_{1+2x}Mn_2O_7$ system, the bilayered crystal is made up of MnO_2 bilayers stacked along the *c* axis and separated by insulating nonmagnetic $(La,Sr)_2O_2$ layers, bringing a quasi-two dimensional structure.[7,8] Due to the reduced dimensionality, the magnetic correlations and competitions in such compounds between the various degrees of freedom (charge, lattice, and spin) are very different from that in ABO_3 three-dimensional (3D) manganites. In the manganites, the transformation from ferromagnetic to paramagnetic phase has a close relation to the colossal magnetoresistance (CMR) effect.[9–13]

Electron spin resonance (ESR) is a powerful tool in the study of magnetic properties. Valuable information about static and dynamic magnetic correlations in manganites can be gained by performing temperature dependent ESR and analyzing the temperature-dependent parameters, such as the resonance field, the *g* value, the peak-to-peak linewidth, and the resonance intensity. We can explicitly obtain the information about a phase separation, which cannot be obtained through macroscopic magnetic methods. In the present work, ESR is used to study the anisotropy magnetic correlations, phase separations, and phase transitions of the ferromagnetic $(La_{0.8}Eu_{0.2})_{4/3}Sr_{5/3}Mn_2O_7$ single crystal. In addition, magnetization is measured by a Quantum Design superconducting quantum interference device (SQUID) magnetometer.

2. Experiment

The $La_{4/3}Sr_{5/3}Mn_2O_7$ and $(La_{0.8}Eu_{0.2})_{4/3}Sr_{5/3}Mn_2O_7$ single crystals were grown by the floating-zone method in an optical image four-mirror furnace. X-ray diffraction measurement of the powders showed no trace of any secondary phase. The back reflection Laue X-ray diffraction method was used to determine the crystallographic direction. The magnetization measurement was performed by using a Quantum Design SQUID magnetometer, MPMS-7. The ESR measurements were taken at 9.5 GHz (*X* band) in a JEOL ESR spectrometer.

3. Results and discussion

Figure 1 shows the in-plane ESR spectra of the $La_{4/3}Sr_{5/3}Mn_2O_7$ single crystal in the temperature range from 120 K to 364 K. Several temperatures are selected for comparison. When the temperature is higher than Curie temperature $T_C \sim 120$ K, a paramagnetic resonance (PMR) line appears, however the ferromagnetic resonance (FMR) line still survives. The PMR line is centered at 3.2 kOe (the *g* value is close to 2) and the FMR line locates at a lower resonance field. Therefore, above T_C, the system is not in a pure paramagnetic

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phase, the paramagnetic and the ferromagnetic phases coexist. In contrast with the $La_{1-x}Sr_xMnO_3$ oxides,[14,15] Mn^{3+} and Mn^{4+} spins in $La_{4/3}Sr_{5/3}Mn_2O_7$ mainly contribute to the PMR lines. When the temperature decreases, the FMR lines move toward the low-field region, owing to the increase of the local magnetic fields in the crystal. The intensities of the PMR and the FMR lines are used for recognizing the nature of the magnetic ions contributing to the resonance, which is proportional to the number of spins. The inset of Fig. 1 shows the temperature dependence of the FMR intensity. The intensity of the FMR decreases gradually as the temperature increases because some of the FM clusters transform into the PM state. Moreover, we obtain similar ESR results when a dc magnetic field is applied along the c axis direction.

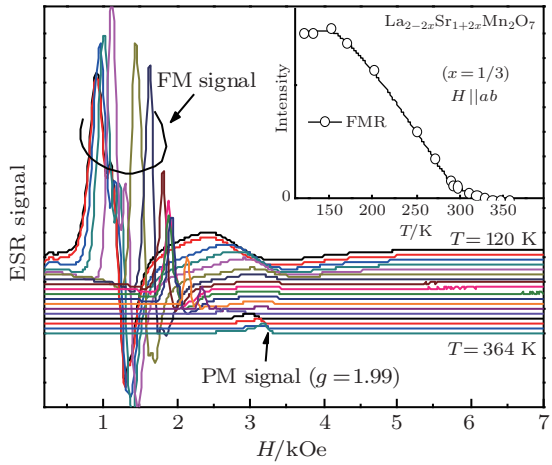


Fig. 1. (color online) ESR spectra of $La_{4/3}Sr_{5/3}Mn_2O_7$ single crystal ($H \parallel ab$ plane). The inset shows the temperature dependence of FMR intensity.

Figure 2 shows the ESR spectra recorded with $H \parallel ab$ plane and $H \parallel c$ axis measured at the temperature range from 300 K to 400 K. The PMR lines are observed in the spectra over the whole experimental temperature range. The PMR line broadens as temperature increases. When the temperature is between 300 K and 350 K, an additional anisotropic FMR line can be clearly identified in both the ab plane and the c axis directions. Above 350 K, the FMR signal becomes very weak and undetectable. It has been assumed that the observed anisotropy of the FMR line is caused by the demagnetization field or by the extant ferromagnetic clusters, if they are large enough.[16] The coexistence of PMR and FMR signals between 300 K and 350 K signifies a phase separation in the temperature range.

By comparing the spectra of the $La_{4/3}Sr_{5/3}Mn_2O_7$ and $(La_{0.8}Eu_{0.2})4_{/3}Sr_{5/3}Mn_2O_7$ single crystals, one can find that the FMR signals become very weak and vanish at the same temperature ($\sim$ 350 K) in both samples. Yang *et al.* have suggested that this temperature (350 K) is a Griffiths temperature T^* and that a Griffiths-like phase exists at $T_C < T < T^*$ in these bilayered manganites.[17] Therefore, we can conclude that a Griffiths-like phase is present below $T^* \sim 350$ K in the Eu doped single crystal.

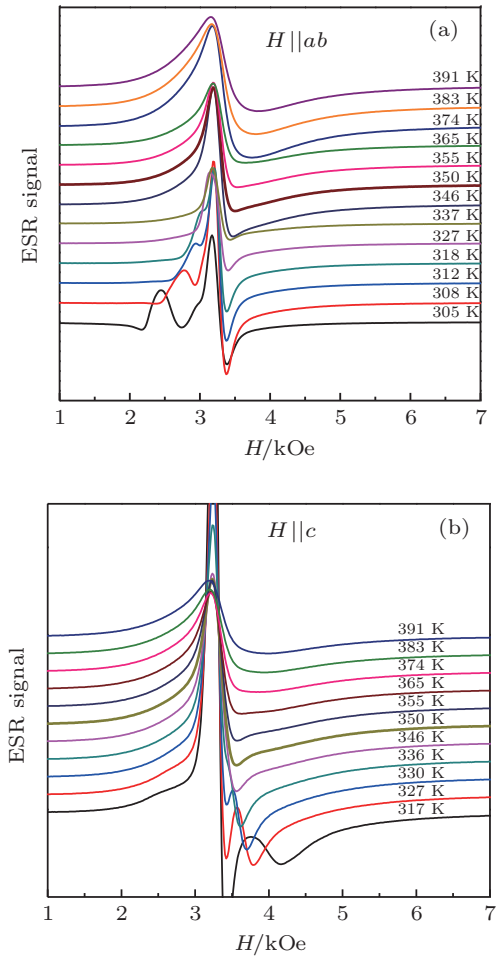


Fig. 2. (color online) ESR spectra of $(La_{0.8}Eu_{0.2})_{4/3}Sr_{5/3}Mn_2O_7$ single crystal: (a) $H \parallel ab$, (b) $H \parallel c$.

If the magnetic field is rotated from the ab plane to the c direction, the PMR lines hardly change with the crystallographic direction, but the FMR lines show obvious anisotropic characteristics. Figure 3 shows the angular variation ESR spectra of $(La_{0.8}Eu_{0.2})_{4/3}Sr_{5/3}Mn_2O_7$ single crystal at 300 K. The magnetic field was rotated from the c axis direction, through the ab plane, and finally to the c axis again. From Fig. 3 we can conclude that the PMR peaks hardly change with the crystallographic direction, while the positions of the FMR peaks change a lot. When the magnetic field is parallel with the ab plane, the FMR peak is the weakest.

We also measured the magnetization of the sample. Figure 4 shows the temperature dependences of the magnetization (M–T curves) under 0.1 T field along the ab plane (M_{ab}) and the c direction (M_c), respectively. ZFC and FC stand for zero field cooling and field cooling, respectively. In both directions, ZFC and FC curves show a distinct bifurcation at the same temperature (about 25 K). The $(La_{0.8}Eu_{0.2})_{4/3}Sr_{5/3}Mn_2O_7$ single crystal changes from the paramagnetic state to a spin-glass-like state and the magnetization is enhanced signifi-

cantly as the temperature increases. Based on the low magnetic field (10 Oe) M–T curve, we can confirm that the spin freezing temperature is $T_f = 29.5$ K. If the splitting occurs only in the c direction, it must be an Ising spin-glass system, such as $Fe_{0.5}Mn_{0.5}TiO_3$ oxides.[18] If the splitting occurs only in the ab plane, it must be an XY-type spin-glass system, such as $Eu_{0.5}Sr_{1.5}MnO_4$ oxides.[19] Because the splitting occurs in both directions, it can be concluded that $(La_{0.8}Eu_{0.2})_{4/3}Sr_{5/3}Mn_2O_7$ is a two-dimensional Heisenberg spin-glass system.[20,21] When fewer Eu^{3+} ions are substituted in the La sites, the Jahn–Teller distortion increases. In the Eu^{3+} ion-rich region, MnO_6 octahedra elongate along the c axis. This change of the crystal field causes outer electrons of the Mn^{3+} ions to favor the $d_{3z^2-r^2}$ orbit, which parallels the c axis. This will weaken the ferromagnetic coupling, and the spin glass phase will eventually appear.[22,23]

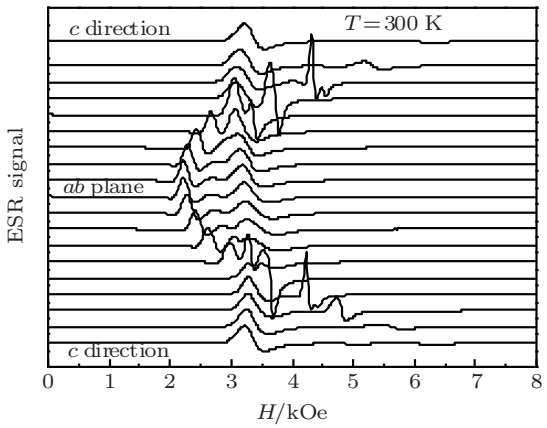


Fig. 3. Angular variation ESR spectra of single-crystal $(La_{0.8}Eu_{0.2})_{4/3}Sr_{5/3}Mn_2O_7$ at room temperature.

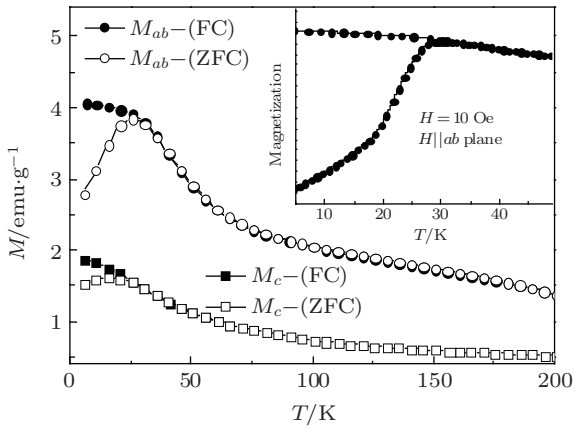


Fig. 4. The M–T curves for $(La_{0.8}Eu_{0.2})_{4/3}Sr_{5/3}Mn_2O_7$ taken at $H =$ 1 kOe. ZFC and FC represent zero-field cooling and field cooling, respectively. The inset shows M–T for $(La_{0.8}Eu_{0.2})_{4/3}Sr_{5/3}Mn_2O_7$ in a 10 Oe field with $H \parallel ab$.

4. Conclusion

We performed a systematic ESR study on $La_{4/3}Sr_{5/3}Mn_2O_7$ and $(La_{0.8}Eu_{0.2})_{4/3}Sr_{5/3}Mn_2O_7$ single crystals. For $(La_{0.8}Eu_{0.2})_{4/3}Sr_{5/3}Mn_2O_7$ single crystal, the PM–FM transitions are well identified from the ESR spectra in both the ab plane and the c axis directions. Above 350 K, the compounds are paramagnetic. For 300 K$< T <$ 350 K, the PM and the FM phases coexist in the system. The phase separation is evidenced for $(La_{0.8}Eu_{0.2})_{4/3}Sr_{5/3}Mn_2O_7$ single crystal. The magnetization measurement reveals a two-dimensional Heisenberg type spin-glass-like behavior below the spin freezing temperature T_f ($\sim$ 29.5 K).

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