Ferromagnetic spin fluctuations in antiferromagnetic Pr$_{1-x}$Ca$_x$MnO$_3$: An ESR study

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Abstract

Electron spin resonance (ESR) measurements have been performed on polycrystalline samples of Pr$_{1-x}$Ca$_x$MnO$_3$ ($x = 0.4, 0.5$) in the temperature range of 100–300 K. The temperature dependence of ESR intensity, $g$ value and linewidth shows the existence of ferromagnetic spin correlations in the paramagnetic state. With decreasing temperature, the ferromagnetic spin correlations switch to antiferromagnetic spin correlations in the charge ordering state and vanish at the antiferromagnetic ordering temperature $T_N$.

1. Introduction

In hole-doped perovskite manganites R$_{1-x}$A$_x$MnO$_3$ (where R and A stand for rare-earth and alkaline-earth metal elements, respectively), the ferromagnetic (FM) metallic state has been qualitatively explained with the double exchange (DE) model [1]. This model implies that the FM spin correlation must be the characteristic feature of spin fluctuations in the paramagnetic (PM) state of doped manganites, regardless of its FM or antiferromagnetic (AFM) ordering in the ground state. When the charge ordering (CO) is formed, however, it suppresses the hopping of the holes, and the FM fluctuations. The FM spin fluctuation in the PM state has been observed in many charge-ordered manganites, including insulating AFM Pr$_{1-x}$Ca$_x$MnO$_3$ [2,3]. Its transport, optical and magnetic properties are all well characterized [4,5]. Furthermore, the long-range AFM ordering establishes at temperatures much lower than $T_{CO}$, this is convenient to examine the mechanism of the switching of spin fluctuations. Neutron scattering studies on Pr$_{1-x}$Ca$_x$MnO$_3$ have confirmed that FM spin fluctuations exist in the PM phase, and they change over to the AFM spin fluctuations below the onset of CO [6,7].

In this work, we try to investigate the spin fluctuations in Pr$_{1-x}$Ca$_x$MnO$_3$ system with electron spin resonance (ESR). ESR has been proved to be a useful tool for the study of magnetic correlations in magnetic materials. It is sensitive to the magnetic interactions and spin correlations through the characteristic behaviors of the ESR resonance field, intensity and linewidth across the transitions. Several ESR studies on Pr$_{1-x}$Ca$_x$MnO$_3$ have been reported [8,9]. However, there have been no systemic ESR studies on the FM spin fluctuations in the PM state and spin fluctuations switching in the CO state. Here, we report the ESR study of Pr$_{1-x}$Ca$_x$MnO$_3$ ($x = 0.4, 0.5$) at temperatures between 100 and 300 K. The analysis of the ESR spectra of both samples reveals a clear switching of the spin fluctuations from the FM spin fluctuation to the AFM one. Our result also suggests that the ESR is a powerful tool to study the magnetic correlations and phase transition in manganites.

2. Experimental details

Polycrystalline samples of Pr$_{1-x}$Ca$_x$MnO$_3$ ($x = 0.3, 0.4$ and $0.5$) were synthesized by the conventional solid-state reaction method. X-ray diffraction patterns of the samples confirmed a single phase in a Pbnm space group. The magnetic measurements were performed using a superconducting quantum interface device magnetometer (Quantum Design MPMS-7). The ESR experiments were carried out on a JEOL JES-FA200 ESR spectrometer at X-band frequencies ($v \approx 9.4$ GHz) with temperature range from 100 to 300 K. The samples were powdered to avoid the skin effects.

3. Results and discussion

Fig. 1 shows the typical ESR spectra for the two compositions recorded in the temperature range from 100 to 300 K, across the...
CO temperature $T_{CO}$ and AFM ordering $T_N$. For both samples, the spectrum consists of a single broad Lorentzian line in the experiment temperature range. Below 100 K, the ESR signals are too weak to be recorded. All the spectra were analyzed by fitting the data to the Lorentzian line shape function \[ \frac{dP}{dH} = \frac{d}{\Delta H_{pp}} + \frac{\Delta H_{pp}}{\Delta H_{pp} + (x - H)^2} \] (1)

where $\Delta H_{pp}$ is the peak to peak linewidth, $H_r$ is the resonance field, $A$ is the area under the absorption curve. The line shape parameters, viz., the intensity, the resonance field and the linewidth are extracted from the fits.

The temperature dependence of $g$ value evaluated from the resonance field for two compositions is shown in Fig. 2. Below 300 K, the $g$ value is not constant but increases gradually with decreasing temperature. This increase of $g$ value in the PM state has been observed in other manganites, and was attributed to the presence of spin correlations in the PM state. As temperature decreases from $T_{CO}$ to $T_N$, the $g$ value decreases gradually. This decrease of $g$ value shows that the FM spin correlations are weakened in the CO state. These results are consistent with the neutron scattering results [6,7], which shows that the FM spin fluctuations exist in the PM phase and they are weakened in the CO state. With further cooling below $T_N$, an abrupt increase of $g$ value was observed. This up-shift may be assigned to a change of spin–orbit coupling [11]. The temperature dependence of $g$ value clearly indicates the coexistence of FM in the PM state and they are weakened with decreasing temperature in the CO state.

Fig. 3 shows the temperature dependence of the ESR intensity for the two compositions. For both the samples, the intensity initially increases with decreasing temperature and shows a broad peak at $T_{CO}$, then decrease with further decreasing temperature in the CO phase. This behavior is observed in other CO manganite as well and also qualitatively similar to the dc susceptibility data measured at 3.2 kOe, shown in the inset of Fig. 1. Neutron scattering on charge-ordered manganites [6,7] have shown that FM spin fluctuations exist in the PM phase, which are progressively replaced by the AFM spin fluctuations as the system goes into the CO state. Thus, the broad peak of the intensity is due to the competition of the FM correlations and AFM correlations as the system goes into the CO state from the PM state, whereas the large decrease below $T_{CO}$ can be attributed to the development of AFM correlations. 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 by neutron scattering, which showed that the FM fluctuation decreases rapidly at the onset of the charge ordering. It remains finite for $T_N < T < T_{CO}$ with little temperature dependence, and then it vanishes completely when the system goes into entirety AFM ground state. Thus, the rapid decrease of intensity below $T_N$ is attributed to the disappearance of FM spin fluctuations on further cooling.
It is noted that in the $x = 0.5$ sample, the AFM ordering is not observed clearly both in the magnetization and the ESR intensity. This is due to the weaker FM spin correlations in the $x = 0.5$ sample. According to the neutron scattering results, the FM correlations for $T_N < T < T_{CO}$ becomes weaker as the hole concentration $x$ approaches the commensurate value $\frac{1}{2}$, but a finite amount of the intensity persists even for the $x = 0.5$ sample. The ESR intensity shows very similar results with the neutron scattering results. This relative high field ($H = 3.2$ kOe) might have suppressed the competition of FM and AFM phases and leads to the absence of clear phase transition in the temperature dependence of magnetization curve.

Fig. 4 shows the temperature dependence of ESR linewidth $\Delta H_{pp}$ for both compositions. As temperature decreases from 300 K, the linewidth $\Delta H_{pp}$ decreases monotonically down to $T_{CO}$ and goes through a minimum near $T_{CO}$. With temperature further decreasing to $T_N$, the linewidth increases significantly and shows a peak near $T_N$. This behavior has been observed in other manganites across the PM insulator-to-FM metal transition, implying a build-up of spin correlations at magnetic ordering. Thus, this sharp increase can be attributed to the building up of spin correlations preceding the CO transition to the long-range AFM ordering, and suggests the formation of precursor AFM order at 160 K. With further cooling, an abrupt decrease of the linewidth is observed, suggesting that the spin correlation is weakened at low temperature below $T_N$.

4. Conclusion

We have studied the Pr$_{1-x}$Ca$_x$MnO$_3$ ($x = 0.4, 0.5$) with dc magnetization and ESR measurement in the temperature range of 100–300 K, across the CO transition temperature ($T_{CO}$) and AFM ordering temperature ($T_N$). The temperature dependence of ESR parameters, including the intensity, $g$ value and linewidth, shows the existence of FM spin correlations in the PM state. The FM correlations decay in the CO state and change over to the AFM spin correlations as temperature approaches $T_N$. Our results also suggest that ESR are powerful tool to study the magnetic correlations in manganites.

References