Evidence for local moments by electron spin resonance study of polycrystalline $LaFeAsO_{1-x}F_x$ ($x=0$ and 0.13)

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The temperature dependence of electron spin resonance was studied in the oxypnictide superconductors $LaFeAsO_{1-x}F_x$ ($x=0$ and 0.13). In the samples, the ESR signal indicates that the g factor and peak-to-peak linewidth strongly depend on temperature, especially at low temperatures. It indicates a strong-coupling picture with existence of local moment. The dependence mentioned above gradually attenuates and tends to saturation around room temperature. This behavior could be ascribed to the "bottleneck" effect due to coupling of local moments and itinerant electrons. In addition, a Curie-Weiss-type behavior is also observed in temperature-dependent spin susceptibility. Our results strongly support the existence of local moments in these materials, while their origin is still unclear. The results also indicate strong magnetic frustration in this system, and the magnetic fluctuation mechanism for superconductivity is suggested.

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The discovery of Fe-based high T_c superconductors provides a new material base to explore the mechanism of high-T_c superconductivity besides high-T_c cuprate superconductors.[1–5] Similar to cuprates, such pnictide superconductors are also believed to have a quasi-two-dimensional (quasi-2D) conducting layer—an Fe_2As_2 layer, which is separated by an LnO (Ln=La, Sm, etc.) or R (R =Ba, Sr, etc.) charge reservior. With doping electron or hole, the ground state of FeAs compounds evolves from a spin-density-wave (SDW) state to a superconducting (SC) state. Electronic phase diagrams of FeAs compounds were also found to be similar to the high-T_c cuprates,[1,6–11] where strong electron-electron coupling is believed to be the key to understand high-T_c superconductivity. Therefore, one may naturally ask whether it is still the case in iron pnictides. As we know, strong in-site Coulomb interaction can produce local moment in cuprates. The existence of local moment is believed to be strong evidence for strong coupling. In FeAs parent compounds, the magnetic moment of Fe^{2+} ion is theoretically predicted to be $(2.4-2.6)\mu_B$,[12–14] while neutron results show a smaller magnetic moment about $(0.36-0.87)\mu_B$.[9,15–18] Moreover, the static susceptibilities for parent compounds decrease with decreasing temperature and show a linear temperature behavior above the SDW transition.[19–21] These results challenge the strong-coupling picture. In this paper, we studied temperature dependence of electron spin resonance (ESR) for $LaFeAsO_{1-x}F_x$ ($x=0$ and 0.13). The benefit of ESR is that it can give us dynamic magnetic information of the local moment. An intrinsic resonance signal was observed, and the g factor and peak-to-peak linewidth show strong temperature dependence in the low-temperature region for the samples. It indicates the existence of the local moment, being consistent with the strong-coupling picture. Further, the "bottleneck" effect due to coupling between local moments and itinerant electrons was also observed in the high-temperature region. In addition, a Curie-Weiss-type behavior in the temperature-dependent spin susceptibility was observed. These results strongly support the strong-coupling picture.

Polycrystalline samples with nominal composition $LaFeAsO_{1-x}F_x$ ($x=0$ and 0.13) were synthesized by conventional solid-state reaction using high purity LaAs, LaF_3, Fe, and Fe_2O_3 as starting materials. LaAs was obtained by reacting La chips and As pieces at 600 °C for 3 h and then 900 °C for 5 h. The raw materials were thoroughly grounded and pressed into pellets. The pellets were wrapped up by Ta foil and sealed in an evacuated quartz tube. They were then annealed at 1160 °C for 40 h. The sample preparation process except for annealing was carried out in a glove box in which the high pure argon atmosphere is filled. The x-ray diffraction (XRD) results show that the samples with $x=0$ are single phase. A tiny but noticeable trace of impurity phase LaOF was observed in $x=0.13$. The ESR measurements of the powder samples were performed using a Bruker ER-200D-SRC spectrometer, operating at X-band frequencies (9.47 GHz) and between 110 and 350 K. The resistance was measured by an ac resistance bridge (LR-700, Linear Research). Magnetic-susceptibility measurements were performed with a superconducting quantum interference device magnetometer in a magnetic field of 7 T. It should be addressed that all results discussed as follows are well reproducible.

Figure 1 shows the temperature dependence of resistivity and magnetization for $LaFeAsO_{1-x}F_x$, with $x=0$ and 0.13. For parent compound LaFeAsO, temperature dependence of resistivity shows a peak around 155 K due to structural transition, and the magnetization also shows a kink and at the same temperature as reported previously.[1] For the F-doped sample, superconductivity with $T_c=26$ K was observed in resistivity and magnetization as shown in Fig. 1. These results show that the electric and magnetic properties of samples used here is consistent with previous works,[1] indicating a good starting point for the ESR study.

Temperature dependences of ESR spectra for $x=0$ and 0.13 samples in the temperature range from 110 to 350 K are shown in Fig. 2. In Figs. 2(a) and 2(b), a tiny background from the secondary phase (e.g., FeAs) in samples was subtracted from the ESR spectra. The raw data without subtract-

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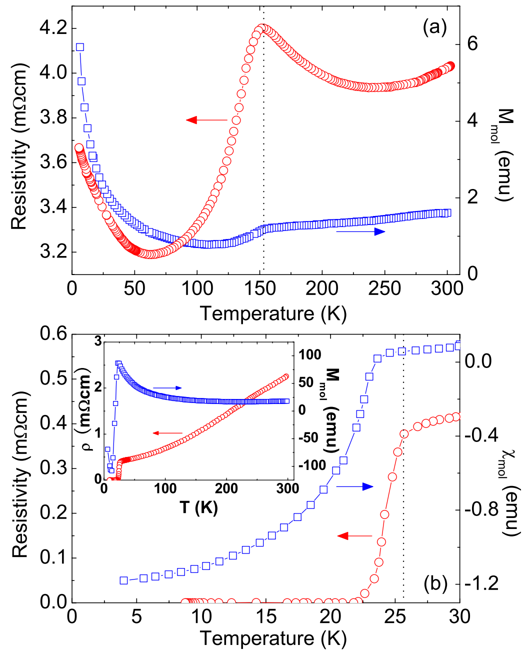

FIG. 1. (Color online) Temperature dependence of resistivity and magnetization for $LaFeAsO_{1-x}F_x$; (a) $x=0$ and (b) $x=0.13$. Magnetization in (a) and inset of (b) are measured with $H=1$ T and susceptibility in (b) is measured with $H=10$ Oe.

ing the background are shown in Figs. 2(c) and 2(d). A well-defined paramagnetic signal was observed for the $x=0$ and 0.13 samples. The Lorentz formula was used to fit the resonance signal very well. As shown in Fig. 2, the linewidth is broadened and the resonance field shifts to the lower end with decreasing temperature. In traditional metal, no obvious paramagnetic resonance signal is expected due to rapid spin-lattice relaxation.[22,23] The observed resonance here should be considered to arise from the local moment. In addition, we have tested the possible effect from the impurities. Such a paramagnetic resonance signal was absent for all impurities at room temperature. It proves that the observed signal is intrinsic for this system.

Figure 3 shows temperature dependence of the g factor and peak-to-peak linewidth (ΔH_{pp}) for the $x=0$ and 0.13 samples. ΔH_{pp} is defined as the width between the highest point and the lowest point in the temperature-dependent ESR spectrum. The resonance field (H_c) to calculate the g factor is defined as the magnetic field corresponding to the midpoint between the highest and lowest points in the ESR spectrum. The g factor is calculated by the following formula: $g=\frac{h\nu}{\mu_B H_c}$. For the parent compound, the g factor monotonously increases with decreasing temperature below 300 K where a linear fitting works well. When temperature exceeds 300 K, the g factor is saturated. In Fig. 3(b), the g factor of the F-doped sample shows a similar behavior. Compared to the parent compound, a clearer trend of g-factor saturation is presented above 260 K for the F-doped sample. Temperature-dependent ΔH_{pp} also shows a similar behavior for the two samples. An upturn behavior appears below 250 K for the $x=0$ sample and 200 K for the $x=0.13$ sample, respectively. Above the upturn temperature, the ΔH_{pp} is saturated with

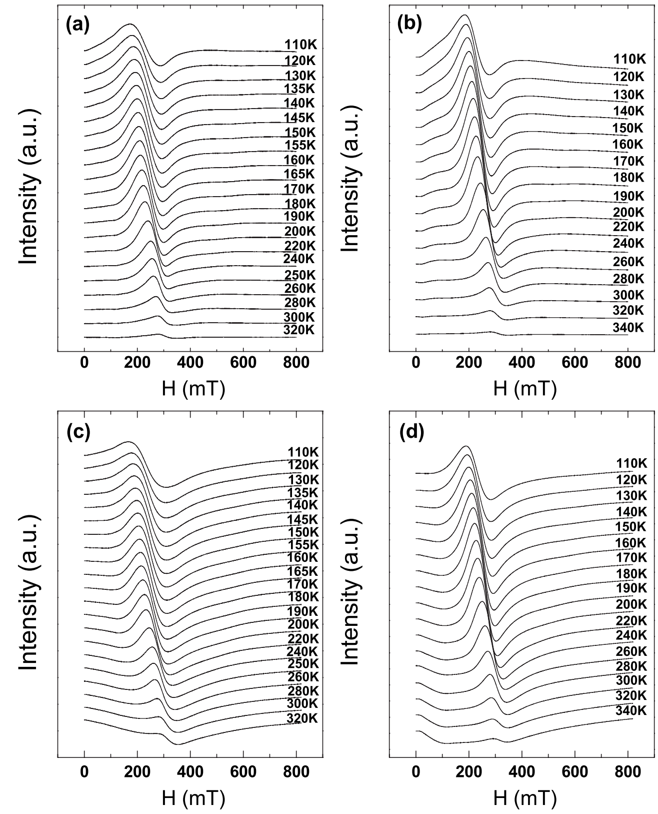

FIG. 2. ESR spectrum with subtracting background under different temperature for (a) $x=0$ and (b) $x=0.13$. (c) and (d) are raw data without subtracting background from ESR spectrum for (a) and (b), respectively.

increasing temperature in the two samples. The amplitude of ΔH_{pp} for $x=0$ is almost the same as that of the $x=0.13$ sample above upturn temperature and becomes larger below upturn temperature. It should be emphasized that the strong temperature dependence of the g factor and ΔH_{pp} cannot be accounted for the paramagnetic local moment because g_{eff} $(=g_s+\Delta g)$ is temperature independent, while linewidth

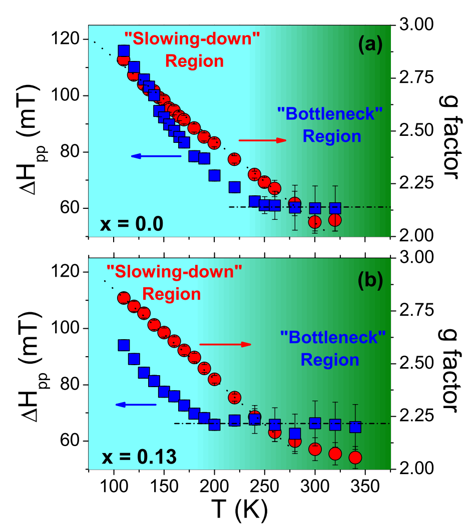

FIG. 3. (Color online) Temperature dependence of g factor and ΔH_{pp} for (a) $x=0$ and (b) $x=0.13$.

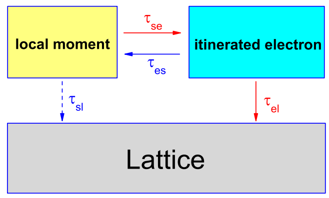

FIG. 4. (Color online) Cartoon model for ESR bottleneck effect showing the various relaxation paths.

$1/\tau$ $(=a+bT)$ follows linear temperature behavior for the system with paramagnetic local moment. The strong temperature-dependent g factor and ΔH_{pp} observed in the ESR spectrum here has been explained by magnetic fluctuation in the system with magnetic phase transition.[22,23] It suggests that magnetic fluctuation from local moments exists in the $LaFeAsO_{1-x}F_x$ ($x=0$ and 0.13) system. Therefore, the question is naturally proposed: how to understand the origin of the local moment. One possible explanation is that local spins from defects in the FeAs layer lead to paramagnetic resonance observed above. As shown in dc magnetization, a Curie-tail behavior is observed in the low temperature for the parent compound. By fitting the data with the Curie-Weiss formula, it is found that the number of $S=1/2$ local spins is about $\sim$0.02 per Fe site and the Curie-Weiss temperature is about $\sim$4 K. In this situation, a very weak intensity of paramagnetic resonance is expected at room temperature because the intensity is proportional to dc magnetization from local spin (about $\sim$0.02 per Fe site). Such an expectation is in sharp contrast to the above observation. In addition, the g factor is much larger than 2 as in the free electron's case, as shown in Fig. 3. Therefore, it indicates that the local spin from defects can be ruled out, and the local moment should come from the Fe atom. But the magnetic state of Fe is still unclear. If local moments exist in a metal, a so-called bottleneck effect takes place in the transfer energy between the spin subsystems.[22,23] Figure 4 shows a cartoon picture for understanding the bottleneck effect. τ_{se} and τ_{es} are the relaxation times between local moments and itinerated electrons, respectively. τ_{el} is the spin-lattice relaxation time for itinerated electrons. τ_{sl} is the spin-lattice relaxation time for local moments. Usually, the local spins are adiabatic for the lattice and the corresponding relaxation path is closed for local moments. When $\tau_{se} > \tau_{el}$, the magnetic energy of local moments can efficiently be passed on to the lattice by itinerated electrons, and the effective relaxation of local moments is determined by relaxation time τ_{se}. When $\tau_{se} < \tau_{el}$, magnetic energy of local moments, which is transferred to itinerated electrons, is quite likely to be returned back rather than passed on to the lattice. Consequently, the relaxation process of the system is dominated by slow relaxation τ_{el}. The latter is called the bottleneck effect. This effect is successfully used to explain the peculiar ESR features in $La_{1-x}Ca_xMnO_3$ and $La_{2-x}Sr_xCuO_4$ systems in which local moments and itinerated electrons come from the same atoms.[24,25] The bottleneck effect is also expected in our system and can be used to understand the high-temperature behavior of the g factor and ΔH_{pp}. The saturation of the g factor and ΔH_{pp} with increasing temperature indicates that the bottleneck effect gradually dominates with increasing temperature, which is similar to the observed results in $La_{1-x}Ca_xMnO_3$ and $La_{2-x}Sr_xCuO_4$.[24,25] Since the intensity of the ESR signal decreases to the limit of the apparatus at high temperatures, a clearer evidence of the bottleneck effect is lack in high temperature. But an increasing ΔH_{pp} and almost invariable g factor are expected, which are observed in many bottleneck systems.[24,25] At low temperatures, the strong ferromagnetic fluctuation ($g \gg 2$) frustrates the relaxation between local moments and itinerated electrons and makes the corresponding relaxation slow down. With decreasing temperature, the bottleneck effect is broken and a strong ferromagnetic fluctuation between local moments enhances the g factor and ΔH_{pp}. These results show that there exists a ferromagnetic fluctuation from local moments. However, an antiferromagnetic order is established below 135 K. It seems that dynamic magnetic properties observed here are very different from static magnetic properties.

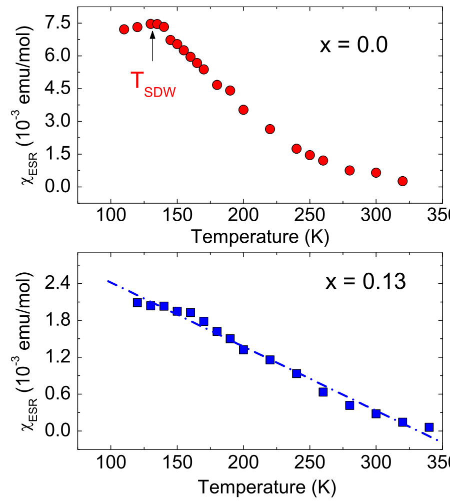

FIG. 5. (Color online) Temperature dependence of spin susceptibility deduced from ESR spectrum. Top panel: $x=0$; bottom panel: $x=0.13$.

Figure 5 shows the temperature dependence of spin susceptibility deduced from the ESR spectrum for both $x=0$ and 0.13 samples, which is proportional to the corresponding integral intensity of the ESR spectrum. For the $x=0$ sample, a Curie-Weiss-type behavior was observed for the high-temperature region and a kink is observed around 135 K which corresponds to the temperature of the spin-density-wave transition determined by neutron scattering. Below 135 K, the intensity of the $x=0$ sample decreases with decreasing temperature due to antiferromagnetic transition. The effective magnetic moment by fitting above the curve with Curie-Weiss formula is about $2\mu_B$, which is close to the theoretical value[12–14] rather than the neutron result.[15] This result also supports that the resonance should be originated from the local moment of the Fe atom. For the F-doped superconducting sample, the Curie-Weiss-type behavior is weakened and the Curie-Weiss fitting is also failed in this situation. A linear behavior is observed in the whole temperature region. However, the value of spin susceptibility is still very large compared to conventional metal without local moment, which is consistent with static magnetization data. Therefore, our above results are both consistent with local-moment pictures.

Recently, the origin of magnetic order in FeAs superconductors is a very hot issue. Two distinct classes of theories have been proposed: local-moment antiferromagnetic ground state for strong coupling[13,26–31] and itinerant ground state for weak coupling.[32–37] The local-moment magnetism approach stresses on-site correlations and assumes that the system is proximity to a Mott insulating state and the resemblance to cuprates; while the latter approach emphasizes the itinerated electron physics and the interplay between the competing ferromagnetic and antiferromagnetic fluctuations. The observed results here may shed light on this debate. First, a "local-moment" effect is observed. The bottleneck effect, Curie-Weiss-type behavior for χ_{ESR}, and strong temperature dependence of the g factor and ΔH_{pp} strongly support the existence of local moments. And the effective magnetic moment is about $2\mu_B$, which is consistent with the theoretical value. Second, ferromagnetic fluctuation is observed among local moments. Our results seem to favor the strong-coupling picture. But it is very strange that there exists a ferromagnetic fluctuation among local moments above the temperature of antiferromagnetic ordering. Kohama *et al.*[38] observed a large Wilson ratio in $LaFeAsO_{1-x}F_x$, indicating ferromagnetic fluctuation in this system. Recently, Zhang *et al.*[39] proposed a "performed SDW moment scenario" to explain the linear temperature behavior in dc magnetization. It results from the existence of a wide fluctuation window in which the local spin-density-wave correlation exists but the global directional order has not yet been established. The so-called local moment is defined as performed SDW moment in this model. If we follow the above idea, the observed ferromagnetic coupling could be understood in a way that there exists a wide ferromagnetic fluctuation window and it coexists and competes with antiferromagnetic fluctuation. Therefore, strong magnetic frustration may be hidden in this system. It could be also used to understand the discrepancy of effective magnetic moment between the neutron result and our ESR result. This maybe shed light to understand the novel magnetic state in the parent compound. On the other hand, although the ΔH_{pp} decreases with F doping, a similar behavior of the g factor and ΔH_{pp} is observed in the parent compound and F-doped superconducting compound, and it indicates that strong magnetic frustration is present in the superconducting sample and magnetic fluctuation may be very important to understand superconductivity in this material. A similar result is also obtained in dc magnetization for polycrystalline $LaFeAsO_{1-x}F_x$.[21]

In conclusion, we study temperature dependence of ESR for $LaFeAsO_{1-x}F_x$ ($x=0$ and 0.13). A strong temperature-dependent g factor and ΔH_{pp} are observed at low temperatures for the samples. Curie-Weiss-type behavior is observed in the temperature-dependent spin susceptibility, and the effective magnetic moment is about $2\mu_B$. These results strongly support the existence of local moments in these materials, but their origin is still unclear (e.g., performed SDW moment). Strong magnetic frustration exists in both the parent compound and superconducting sample. Magnetic fluctuation plays an important role in the mechanism for superconductivity.

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