Phase Diagram and Quantum phase transition in Newly Discovered Superconductors: $SmO_{1-x}F_xFeAs$

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The magnetic fluctuations associated with a quantum critical point (QCP) are widely believed to cause the non-Fermi liquid behaviors and unconventional superconductivities, for example, in heavy fermion systems and high temperature cuprate superconductors. Recently, superconductivity has been discovered in iron-based layered compound $LaO_{1-x}F_xFeAs$ with $T_c=26$ K\cite{1}, and it competes with spin-density-wave (SDW) order\cite{2}. Neutron diffraction shows a long-range SDW-type antiferromagnetic (AF) order at $\sim 134$ K in LaOFeAs\cite{3, 4}. Therefore, a possible QCP and its role in this system are of great interests. Here we report the detailed phase diagram and anomalous transport properties of the new high-Tc superconductors $SmO_{1-x}F_xFeAs$ discovered by us\cite{5}. It is found that superconductivity emerges at $x \sim 0.07$, and optimal doping takes place in the $x \sim 0.20$ sample with highest $T_c \sim 54$ K. While $T_c$ increases monotonically with doping, the SDW order is rapidly suppressed, suggesting a QCP around $x \sim 0.14$. As manifestations, a linear temperature dependence of the resistivity shows up at high temperatures in the $x < 0.14$ regime, but at low temperatures just above $T_c$ in the $x > 0.14$ regime; a drop in carrier density evidenced by a pronounced rise in Hall coefficient are observed, which mimic the high-$T_c$ cuprates. The simultaneous occurrence of order, carrier density change and criticality makes a compelling case for a quantum critical point in this system.

Since the discovery of high-transition temperature ($T_c$) superconductivity in layered copper oxides, extensive efforts have been devoted to explore the higher $T_c$ superconductivity. Very recently, layered rare-earth metal oxypnictides LnOMPn (Ln=La, Pr, Ce, Sm; M=Fe, Co, Ni, Ru and Pn=P and As) with ZrCuSiAs type structure\cite{8, 9} have attracted great attention due to the discovery of superconductivity at $T_c = 26$ K in the iron-based $LaO_{1-x}F_xFeAs$ ($x=0.05-0.12$)\cite{1}. Immediately, $T_c$ was drastically raised to 43 K in $SmO_{1-x}F_xFeAs$\cite{5}, followed by reports of $T_c=41$ K in $CeO_{1-x}F_xFeAs$\cite{6}, and 52 K in $PrO_{1-x}F_xFeAs$\cite{7}. These discoveries have generated much interest for exploring novel high temperature superconductor, and provided a new material base for studying the origin of high temperature superconductivity. The superconductivity in these materials appears to be unconventional, and much careful work will be required to elucidate the interesting physics here. It appears that the electron-phonon interaction is not strong enough to give rise to such high transition temperatures\cite{10}, while strong ferromagnetic and antiferromagnetic fluctuations have been
proposed to be responsible\textsuperscript{11, 12, 13}.

The undoped material LaOFeAs has been reported to undergo a spin density wave (SDW) transition at 150 K\textsuperscript{1, 2}. The SDW is suppressed and superconductivity emerges with increasing F doping\textsuperscript{2}. Systematical characterizations for evolution of the superconductivity and SDW with F-doping are important for understanding the underlying physics. Here we successfully prepared a series of $SmO_{1-x}F_xFeAs$ samples with $x = 0 \sim 0.3$ and systematically studied their resistivity and Hall coefficient, and gave its phase diagram. The resistivity shows clear anomaly and the Hall coefficient increases sharply at temperature $T_s \sim 148$ K for SmOFeAs, indicating the onset of spin-density wave. $T_s$ was found to decrease with increasing doping, manifesting the competition between superconductivity and SDW. A crossover occurs around $x \sim 0.14$ for $T$–linear dependence of resistivity from in high temperature range to in low temperature range (just above $T_c$) with increasing doping. The drop in carrier density and a T-linear dependence of the resistivity are two hallmarks of a quantum phase transition in metals \textsuperscript{14}, strongly suggesting existence of a quantum critical point in this system.

Polycrystalline samples with nominal composition $SmO_{1-x}F_xFeAs$ (x=0-0.3) were synthesized by conventional solid state reaction using high purity SmAs, $SmF_3$, Fe and $Fe_2O_3$ as starting materials. SmAs was obtained by reacting Sm chips and As pieces at 600 °C for 3 hours and then 900 °C for 5 hours. The raw materials were thoroughly grounded and pressed into pellets. The pellets were wrapped into Ta foil and sealed in an evacuated quartz tube. They are then annealed at 1160 °C for 40 hours. The sample preparation process except for annealing was carried out in glove box in which high pure argon atmosphere is filled. Figure 1a shows the XRD patterns for the polycrystalline samples $SmO_{1-x}F_xFeAs$ with different $x$. The main peaks in XRD pattern can be well indexed to the tetragonal ZrCuSiAs-type structure. The XRD patterns show that the samples with x=0 and 0.05 are single phase. A tiny but noticeable trace of impurity phases SmOF, Fe and SmAs is observed for $0.12 \leq x \leq 0.20$. Large amount of impurity phases are observed in the samples with $x >0.2$. Fig.1b shows variation of a-axis and c-axis lattice parameters with doping F. It shows that both of a-axis and c-axis lattice parameters decrease systematically with nominal dopant concentration by substitution of $F^-$ for $O^{2-}$. But the lattice constants do no change with beyong $x = 0.2$, suggesting that the chemical phase boundary is reached at $x \sim 0.2$ in $SmO_{1-x}F_xFeAs$ system.
Figure 1c shows the superconducting transition of the resistivity for $SmO_{1-x}F_xFeAs$ system. No superconducting transition is observed down to 5 K for the samples with $x=0$ and 0.05. The $x=0.1$ sample shows an onset transition at $\sim 12$ K, but no zero-resistance is observed down to 5 K. The emergence of superconductivity roughly occurs at $x \sim 0.07$. Superconducting transition temperature increases monotonically with increasing F content up to 0.2, optimal doping takes place in $x=0.2$ sample with highest $T_c \sim 54$ K as shown in Fig.1d. As shown in Fig.1a, large amount of impurity phases shows up for the samples with $x$ larger than 0.2, but these samples with $x$ up to 0.5 still show superconductivity at $\sim 50$ K, which is nearly independent of $x$. It further evidences that the F doping is limited to be about 0.2.

Figure 2 shows the temperature dependence of resistivity in normal state with temperature up to 475 K for the samples $SmO_{1-x}F_xFeAs$ ($x=0$-0.2). The undoped sample shows a similar behavior to that observed in LaOFeAs[1]. An anomalous peak associated with SDW shows up at $\sim 150$ K. Below the occurrence temperature of SDW, the resistivity drops steeply. The temperature corresponding to the peak in resistivity is defined as the formation temperature of SDW ($T_s$). F-doping leads to a suppression of the SDW anomaly peak, and to the shift of $T_s$ to lower temperature. At 10% F-doping, a weak anomaly peak is still observed. Another striking feature is that a linear temperature dependence of the resistivity persists from high temperatures to a characteristic temperature ($T_0$) in the $x \leq 0.10$ range, at which the resistivity deviates from T-linear behavior and increases with decreasing temperature. This should arise from magnetic correlation before formation of SDW. The $T_0$ of undoped sample is about $\sim 290$ K much higher than $T_s \sim 150$ K of the SDW anomaly peak. Such a behavior is very similar to that observed in the "stripe" phase of $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$, where deviation of resistivity from T-linear behavior also occurs at 150 K above the "stripe" formation temperature[15]. In contrast to the case of the samples with $x \leq 0.10$, no SDW anomaly peak is observed in the $x \geq 0.12$ sample, and the resistivity decreases more quickly than the linear behavior below $T_0$, being similar to the pseudogap behavior in high-$T_c$ cuprates[16]. The steep drop in resistivity below $T_s$ has been ascribed to the occurrence of SDW[2].

Remarkably, the low temperature resistivity can be well fitted with $a+bT^n$, and the fitting parameter $n$ shows a systematical change from 2.3 to 1 with increasing F content from $x=0$ to 0.15 (Fig.2). An intriguing observation is that a crossover in temperature dependence of the
resistivity happens between the samples with $x=0.14$ and $x=0.15$. In contrast to the samples with $x \leq 0.13$, the high-temperature resistivity for the samples with $x > 0.14$ does not follow a T-linear behavior but tends to be saturated. However, the temperature dependence of the low-temperature resistivity just above $T_c$ changes to $T$-linear dependence, and the resistivity deviates from the T-linear behavior in high temperatures at certain temperature ($T'_0$). $T'_0$ increases from 130 K for the $x=0.15$ sample to 205 K for the $x=0.20$ sample. These results indicate that a profound change in resistivity takes place around $x \sim 0.14$, suggesting that the complete suppression of SDW occurs and quantum critical point appears around $x=0.14$. Particularly, a possible explanation for T-linear resistivity, that is widely used to explain the T-linear resistivity in heavy-fermion metals[14], is the scattering of charge carriers by fluctuation associated with quantum critical point.

Temperature dependence of Hall coefficient ($R_H$) for the $SmO_{1-x}F_xFeAs$ ($x=0-0.2$) system with $x=0$, 0.05, 0.10, 0.13, 0.15 and 0.20 is shown in Fig.3a and 3b. The Hall coefficient is negative, and decreases with increasing $x$, indicating that F-doping leads to an increase in carrier concentration. Hall coefficient for the samples with $x=0$, 0.05 and $x=0.10$ show a strong temperature dependence at low temperatures. As shown in Fig.3a, Hall coefficient shows a pronounced rise at a certain temperature which coincides with $T_s$ of the SDW anomaly peaks observed in Fig.2. It indicates a drop in carrier concentration at $T_s$ due to the occurrence of SDW. It has been revealed before that Hall coefficient is prominently enhanced if strong antiferromagnetic (or SDW) fluctuations exist in heavy fermion system[17]. The evolution of $R_H$ with $x$ is very similar to the $R_H$ behavior near AF-QCP in the heavy fermion system $CeMn_5$ (M=Co,Rh)[18]. Compared to the behavior of $x=0$, 0.05 and 0.10 samples, Hall coefficient of the $x=0.15$ and 0.20 samples shows much weak temperature dependence, and no clearly pronounced rise at low temperature is observed. Especially, the $x=0.2$ sample shows very weak temperature dependence at low temperature. The Hall angle is plotted as $cot\theta_H = \rho/R_H$ vs $T^{1.5}$ in Fig.3c and 3d. It is remarkable that the data make a straight line in the entire temperature range for the $x=0.13$, 0.15 and 0.20 samples, while in the temperature range above $T_s$ for the $x=0$, 0.05 and 0.10 sample. These results present that there exists a scaling law between the Hall angle and temperature: $cot\theta_H \propto T^{1.5}$. The deviation of Hall angle from $T^{1.5}$ dependence arises from the occurrence of SDW, because the its characteristic temperature is exactly the same as the temperature of the SDW anomaly peak in resistivity. Such behavior is very similar to that observed in high-$T_c$ cuprates where
the Hall angle is proportion to $T^2$[19], and deviation of Hall angle from $T^2$ dependence occurs at the onset temperature of pseudogap[20]. The results of resistivity and Hall coefficient show that a linear temperature dependence of the resistivity and a drop in carrier density as evidence by a pronounced rise in Hall coefficient are associated to the occurrence of spin density wave. Since the T-linear dependence of the resistivity and a drop in carrier density is the characteristic of a quantum phase transition in metals[14], it suggests a quantum critical point around $x=0.14$ due to competing of the SDW state and superconductivity.

Our findings are summarized in the electronic phase diagrams shown in Fig.4, where the characteristic temperatures of $T_s$, $T_0$ and $T'_0$ are also shown. With increasing F-doping, the onset of SDW in Sm(O,F)FeAs system is driven down in temperature, and the superconducting state emerges at $x \sim 0.07$, reaching a maximum $T_c$ of $54$ K at $x=0.20$. Compared to the phase diagram of high-$T_c$ cuprates, no decrease of $T_c$ is observed with increasing doping up to the chemical phase boundary at $x \sim 0.20$. Moreover, there is a large intermediate regime where superconductivity and SDW coexist for Sm(O,F)FeAs. Based on the evolutions of the resistivity with $T$ and $x$ in Fig.2, the different power law dependent behaviors of the resistivity are summarized in Fig.4. One could find drastically different temperature-dependencies of resistivity at two sides of $x=0.14$. On the left side, the $n$, as that used in the $a+bt^n$ to fit the low temperature resistivity, continuously decreases from 2.3 to 1.2 when $x$ is raised from 0 to 0.14 respectively; while on the right side, the $n$ is fixed at 1 for $x > 0.15$. It clearly indicates that SDW eventually disappears around $x \sim 0.14$. More importantly, together with the results of Hall coefficient, it suggests the existence of a SDW quantum critical point, which may be crucial for the mechanism of superconductivity in these iron-based high-$T_c$ superconductors, as being suggested before for the superconductivity in the copper-based ones.

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FIG. 1: (a): X-ray diffraction patterns at room temperature for the samples $SmO_{1-x}Fe_xAs$. (b): Variation of lattice parameters with $x$. (c): Superconducting transitions for the samples $SmO_{1-x}Fe_xAs$ with $x=0$, 0.05, 0.10, 0.12, 0.14, 0.15 and 0.20. (d): Superconducting transition in resistivity and susceptibility for the $x=0.20$ sample with highest $T_c \sim 54$ K.
FIG. 2: Temperature dependence of the resistivity in the normal state up to 475 K for the samples SmO$_{1-x}$F$_x$FeAs with $x=0$, 0.05, 0.10, 0.12, 0.13, 0.14, 0.15 and 0.20. Arrows denote the onset temperature ($T_s$) of spin-density wave and deviating temperatures from T-linear behavior ($T_0$ and $T'_0$). The resistivity shows a linear temperature dependence above $T_0$ for the samples with $x < 0.14$, while a T-linear behavior is observed in the temperature range from $T_c$ to $T'_0$ for the samples with $x > 0.14$. The low temperature resistivity can be well fitted with $a + bT^n$ for all the samples with $x \leq 0.14$, and the $n=2.3$, 2.0, 1.8, 1.6, 1.3, 1.2 for the samples with $x=0$, 0.05, 0.10, 0.12, 1.3, and 1.4, respectively; while low temperature resistivity shows a T-linear behavior for the samples with $x \geq 0.15$. 
FIG. 3: (a): Temperature dependence of Hall coefficient for the samples $SmO_{1-x}F_xFeAs$ with $x=0, 0.05$ and 0.10; (b): Temperature dependence of Hall coefficient for the samples with $x=0.13$, 0.15 and 0.20. A pronounced rise in Hall coefficient is observed for the $x=0$, 0.05 and 0.10 samples. (c): Hall angle is plotted as $\cot\theta_H$ vs $T^{1.5}$ for the samples with $x=0$, 0.05 and 0.10; (d): $\cot\theta_H$ vs $T^{1.5}$ for the samples with $x=0.13$, 0.15 and 0.20. The data points fall on a straight line in the entire temperature range for the $x=0.13$, 0.15 and 0.20 samples, while deviation from the straight line at certain temperature for the $x=0$, 0.05 and 0.10 sample. The deviating temperature from straight line is exactly the same as $T_s$ of SDW anomaly peak observed in Fig.2.
FIG. 4: Electronic phase diagram for $SmO_{1-x}F_xFeAs$ system. $T_s$ indicates the formation temperature of SDW. $T_0$ and $T'_0$ represent the deviating temperature from a T-linear dependence of resistivity in low and high temperatures, respectively. The superconductivity starts to appear at $x \sim 0.07$, reaching a maximum $T_c$ of $\sim 54$ K at $x=0.20$. Compared to the phase diagram of high-$T_c$ cuprates, no decrease of $T_c$ with increasing doping has been observed. It is because the chemical phase boundary is reached at $x \sim 0.20$. The different color regions represent different $n$ in the formula $\rho = a + bT^n$, which can be well used to fitted to the low temperature resistivity shown in Fig.2. The dot line of $x=0.14$ clearly shows a boundary for different behavior of T-dependent resistivity below and above $x=0.14$, suggesting a quantum critical point around $x \sim 0.14$. 