

# Superconductivity at 56 K in Samarium-doped SrFeAsF

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We synthesized the samples  $\text{Sr}_{1-x}\text{Sm}_x\text{FFeAs}$  with ZrCuSiAs-type structure. These samples were characterized by resistivity and susceptibility. It is found that substitution of rare earth metal for alkaline earth metal in this system suppresses the anomaly in resistivity and induces superconductivity. Superconductivity at 56 K in nominal composition  $\text{Sr}_{0.5}\text{Sm}_{0.5}\text{FFeAs}$  is realized, indicating that the superconducting transition temperatures in the iron arsenide fluorides can reach as high as that in oxypnictides with the same structure.

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The recent discovery of superconductivity in oxypnictides with the critical temperature ( $T_C$ ) higher than McMillan limit of 39 K (the theoretical maximum predicted by BCS theory) has generated great excitement[1, 2, 3, 4, 5, 6] since the superconductivity is clearly unconventional compared with in the cuprate superconductors. The high- $T_c$  iron pnictides with ZrCuSiAs-type structure adopt a layered structure of alternating  $(\text{FeAs})^-$  and  $(\text{LnO})^+$  layers with eight atoms in a tetragonal unit cell. Structural phase transition from tetragonal to orthorhombic happens before the antiferromagnetic spin-density-wave ordering.[7, 8] Such transition leads to an anomaly in resistivity. Doping of charge into the system suppresses the structural and magnetic instabilities, and induces superconductivity. Recently, the iron arsenide fluorides  $\text{AEFeAsF}$  (AE=Sr, Ca etc.) with ZrCuSiAs-type structure, where the  $(\text{LnO})^+$  layers in  $\text{LnFeAsO}$  are replaced by  $(\text{AEF})^+$  layer have been reported.[9, 10, 11] Co-doping in  $\text{CaFeAsF}$  leads to a maximum  $T_c$  of 22 K,[9] and a superconducting transition at about 36 K is reported in  $\text{Sr}_{0.8}\text{La}_{0.2}\text{FeAsF}$ .[12]

Here we report the discovery of superconductivity at 56 K in nonnominal composition  $\text{Sr}_{1-x}\text{Sm}_x\text{FeAsF}$  ( $x=0.5$ ) with ZrCuSiAs-type structure. The  $T_c$  is almost the same as the highest superconducting transition temperature observed in F-doped oxypnictide superconductors.

The polycrystalline samples with nominal composition of  $\text{Sr}_{1-x}\text{Sm}_x\text{FeAsF}$  were synthesized by solid state reaction method by using  $\text{SrF}_2$ ,  $\text{SrAs}$ ,  $\text{SmAs}$ , and  $\text{Fe}_2\text{As}$  as starting materials:  $0.5\text{SrF}_2 + (0.5-x)\text{SrAs} + x\text{SrAs} + 0.5\text{Fe}_2\text{As} \rightarrow \text{Sr}_{1-x}\text{Sm}_x\text{FeAsF}$ .  $\text{SrAs}$  was pre-synthesized by heating the mixture of Sr powder and As powder in an evacuated quartz tube at 873 K for 10 hours.  $\text{SmAs}$  and  $\text{Fe}_2\text{As}$  were obtained by respectively reacting the mixture of Sm powder, Fe powder and As powder in evacuated quartz tubes at 1073 K for 10 hours. The raw materials were accurately weighed according to the stoichiometric ratios of  $\text{Sr}_{1-x}\text{Sm}_x\text{FeAsF}$ , then the weighed

powders were thoroughly grounded and pressed into pellets. The pellets were wrapped with Ta foil and sealed in evacuate quartz tubes. The  $\text{SrFeAsF}$  was slowly heated to 1173 K and kept at this temperature for 40 hours and cooled down to room temperature. Then the resultant pellet was grounded again, sealed in a quartz tube for a second sintering at 1273 K for 20 hours. The samples of  $\text{Sr}_{0.8}\text{Sm}_{0.2}\text{FeAsF}$  and  $\text{Sr}_{0.5}\text{Sm}_{0.5}\text{FeAsF}$  were slowly heated to 1273 K for 20 hours, then the products were grounded again, sealed in a quartz tube for a second sintering at 1273 K for 10 hours. The sample preparation process except for annealing was carried out in glove box ( $\text{O}_2, \text{H}_2\text{O} < 1$  ppm) in which high pure argon atmosphere is filled.

The crystal structure of these samples was characterized by X-ray diffraction (XRD) with Rigaku D/max-A X-ray diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda=1.5418\text{\AA}$ ) in the  $2\theta$  range of  $5 - 65^\circ$  with the step of  $0.02^\circ$  at room temperature. Resistivity measurements were performed on a AC resistance bridge (Linear Research Inc., Model LR700) by the standard four-probe method. The measurement of susceptibility was performed in Quantum Design PPMS systems (Quantum Design).

Figure 1 shows X-ray powder diffraction patterns of  $\text{SrFeAsF}$ ,  $\text{Sr}_{0.8}\text{Sm}_{0.2}\text{FeAsF}$  and  $\text{Sr}_{0.5}\text{Sm}_{0.5}\text{FeAsF}$  respectively. All diffraction peaks in the XRD pattern of the sample  $\text{SrFeAsF}$  can be indexed by a tetragonal structure with  $a=0.3995$  nm and  $c=0.8961$  nm, where no impurity peak is observed. It indicates that the samples is single phase. For  $\text{Sr}_{0.8}\text{Sm}_{0.2}\text{FeAsF}$  sample, all the main peaks can be indexed to ZrCuSiAs-type structure with  $a=0.3929$  nm and  $c=0.8958$  nm. Only small amount of impurity phase of  $\text{SrF}_2$  was detected. For  $\text{Sr}_{0.5}\text{Sm}_{0.5}\text{FeAsF}$  sample, the diffraction peaks except for the diffraction peaks from impurity phases of  $\text{SrF}_2$  and  $\text{SmAs}$  can be indexed by a tetragonal structure with  $a=0.3918$  nm and  $c=0.8956$  nm. It is found that Sm doping leads to an apparent decrease in a-axis and a slight

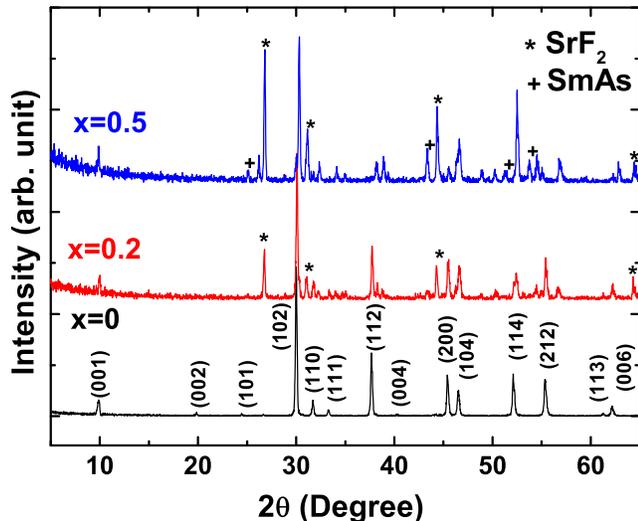


FIG. 1: X-ray diffraction patterns at room temperature for the samples  $\text{Sr}_{1-x}\text{Sm}_x\text{FeAsF}$  with  $x=0, 0.2$ , and  $0.5$ . All diffraction peaks can be indexed with a tetragonal structure for the  $x=0$  sample. However, the impurity phases of  $\text{SrF}_2$  and  $\text{SmAs}$  are observed in  $x=0.2$  and  $0.5$  samples.

contraction of the  $c$ -axis. With increasing Sm doping, impurity phase of  $\text{SrF}_2$  apparently increases. The impurity phase of  $\text{SmF}$  shows up in  $\text{Sr}_{0.5}\text{Sm}_{0.5}\text{FeAsF}$  sample.

Figure 2 shows temperature dependence of resistivity for the samples  $\text{SrFeAsF}$ ,  $\text{Sr}_{0.8}\text{Sm}_{0.2}\text{FeAsF}$  and  $\text{Sr}_{0.5}\text{Sm}_{0.5}\text{FeAsF}$ . The resistivity of  $\text{SrFeAsF}$  shows a clear anomaly in resistivity at about 173 K. While cooling down from temperature, the sample's resistivity grows slightly before 173K, then drops sharply with the temperature continues decreasing. At low temperatures, the resistivity shows a semiconducting behavior. This is consistent with previous reports.[10, 11] The anomaly in resistivity is ascribed to the formation of an SDW order or a structural transition, similar to what's observed in  $\text{LnFeAsO}$  ( $\text{Ln} = \text{rare earth elements}$ ) and  $\text{MFe}_2\text{As}_2$  ( $\text{M} = \text{Ba, Sr}$ ) system. With Sm doping, the anomaly in resistivity is suppressed, and the transition temperature down-shifts to 163 K for  $\text{Sr}_{0.8}\text{Sm}_{0.2}\text{FeAsF}$ , while the semiconducting behavior at low temperature is also suppressed. As shown in Fig.2, a sharp superconducting transition at about 56 K occurs in resistivity for the sample  $\text{Sr}_{0.5}\text{Sm}_{0.5}\text{FeAsF}$ . The resistivity shows a metallic behavior in the whole temperature range and no anomaly appears. It suggests that the SDW order or the structural transition is completely suppressed for the superconducting sample. The behavior of resistivity in the normal state is exactly the same as that observed in superconducting sample  $\text{SmFeAsO}_{1-x}\text{F}_x$  ( $x=0.15$  and  $0.2$ ).[5] It should also be emphasized that no superconducting transition is observed in the sample  $\text{Sr}_{0.8}\text{Sm}_{0.2}\text{FeAsF}$ .

To confirm the superconductivity observed in re-

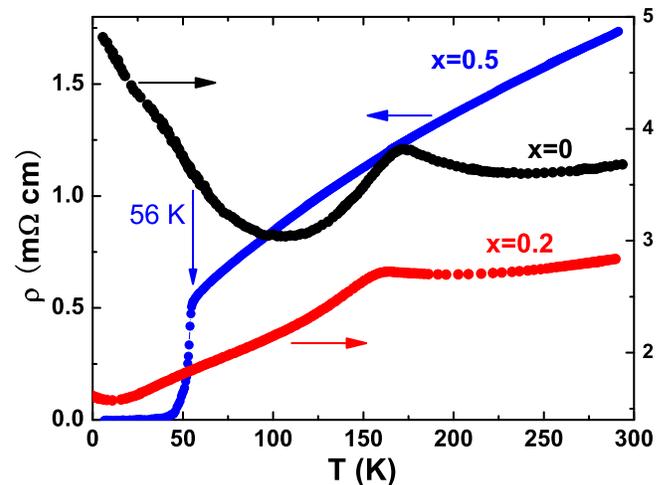


FIG. 2: Temperature dependence of resistivity for the samples  $\text{Sr}_{1-x}\text{Sm}_x\text{FeAsF}$  with  $x=0, 0.2$ , and  $0.5$ . The anomaly in resistivity associated with structural and SDW transitions is suppressed with Sm doping. A sharp superconducting transition at 56 K is observed in the  $x=0.5$  sample.

sistivity for the sample with nominal composition  $\text{Sr}_{0.5}\text{Sm}_{0.5}\text{FeAsF}$ , the susceptibility is measured under 10 Oe in zero-field cooled and field-cooled cycles. Temperature dependence of susceptibility is shown in Fig.3. A clear diamagnetic transition occurs at 53.5 K corresponding to the mid-transition temperature in resistivity, indicating of a bulk superconductivity. It should be pointed out that the superconducting volume is small, and the apparent Meissner fraction is less than 10%, while the resistance goes to zero. The reason could be that there are some magnetic impurities (such as FeAs) in this sample. The magnetic ordering of these impurities may depress the Meissner fraction. The actual Meissner fraction must be larger. Next step is how to synthesize the sample of high purity and improve the superconducting volume fraction. The superconducting phase should be Sm-doped  $\text{SrFeAsF}$  because only impurity phases  $\text{SrF}_2$  and  $\text{SmAs}$  are observed in x-ray diffraction pattern of  $\text{Sr}_{0.5}\text{Sm}_{0.5}\text{FeAsF}$ . These impurity phases are non-superconducting.

In summary, partial substitution of Sr with Sm leads to the suppression of the structural and SDW transition, meanwhile induces superconductivity. The electrical conductivity and magnetization measurements demonstrate a bulk superconductivity at 56 K in a nominal composition of  $\text{Sr}_{0.5}\text{Sm}_{0.5}\text{FeAsF}$ . Our results indicate that it is possible to find superconductivity in other fluorine-arsenide family.

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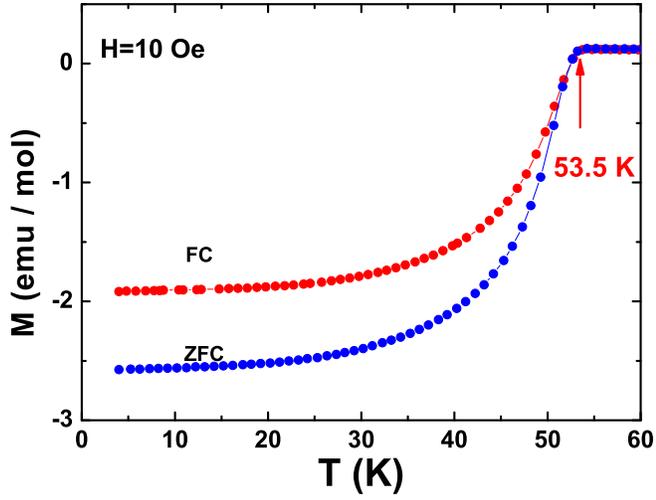


FIG. 3: Temperature dependence of DC magnetization for the sample with nominal composition  $\text{Sr}_{0.5}\text{Sm}_{0.5}\text{FeAsF}$  measured at a DC field of 10 Oe in the zero field-cooled (ZFC) and field-cooled cycles. It indicates a bulk superconductivity.

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