Superconductivity in fluoride-arsenide Sr$_{1-x}$La$_x$FeAsF compounds

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Abstract – By using a two-step solid-state reaction method, we successfully fabricated the new family of fluoride-arsenide AeFeAsF compounds (Ae = alkaline-earth elements, Sr, Eu and Ca) with the ZrCuSiAs structure and with the new building block AeF instead of the REO (both the formal charge of the AeF Layer and the REO layer are “+1”). The undoped parent phase has a Spin-Density-Wave–like transition at about 173 K for SrFeAsF, 118 K for CaFeAsF and 153 K for EuFeAsF. By doping electrons into the system the resistivity anomaly associated with this SDW transition is suppressed and superconductivity appears at 29.5 K (with the criterion of 90% of the normal-state resistivity) in the fluoride-arsenide Sr$_{1-x}$La$_x$FeAsF (x = 0.4). Our discovery here suggests that other new superconductors may be obtained if one uses different rare-earth elements to substitute the alkaline-earth elements in AeFeAsF.

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Introduction. – Since the discovery of superconductivity [1] at 26 K in the oxy-pnictide LaFeAsO$_{1-x}$F$_x$, enormous interests have been stimulated in the fields of condensed-matter physics and material sciences. Among the five different structures in this broad type of superconductors [2–6], the ZrCuSiAs structure has received special attention since the $T_c$ has been quickly promoted to 55–56 K [7–9] in fluorine-doped oxy-pnictides REFeAsO (RE = rare-earth elements). The superconductivity can also be induced by applying a high pressure to the undoped samples [10,11]. The mechanism of superconductivity in the FeAs-based system remains unclear yet, but it turns out to be clear that any change in the structure or the building blocks will lead to a change of the superconducting transition temperatures.

It is known that the F-doped REFeAsO superconductors have a ZrCuSiAs structure (see inset in fig. 1) with the alternative building series of RE$^{3+}$O$_2^-$ and Fe$^{2+}$As$^{3-}$ and the formal charge of the RE$^{3+}$O$_2^-$ layer is “+1”. It thus becomes quite straightforward that one may try different building blocks with the same ionic state of “+1” to substitute REO. The combination of Ae$^{2+}$F$^-$/ with Ae = the alkaline earth elements (Sr, Eu, Ca etc.) may be a good choice. Actually the SrF-based parent compound was fabricated in the copper-sulfur system SrFCuS [12,13] and very recently in the FeAs-based systems [14,15]. Also very recently superconductivity at 22 K was found in CaFe$_{1-x}$Co$_x$AsF [16] and at 4 K in SrFe$_{1-x}$Co$_x$AsF [17]. It was believed that Co doping may introduce electrons into the parent compounds.

In this letter, we report the fabrication of the new family of compounds, namely fluoride-arsenides AeFeAsF with the ZrCuSiAs structure and with the new building block AeF instead of the REO (both the formal charge of the AeF layer and the REO layer are “+1”). The undoped parent phase has a Spin-Density-Wave–like transition at about 173 K for SrFeAsF, 118 K for CaFeAsF and 153 K for EuFeAsF. By doping electrons into the system, the resistivity anomaly associated with this SDW transition is suppressed and superconductivity appears at 29.5 K in the fluoride-arsenide Sr$_{1-x}$La$_x$FeAsF (x = 0.4).

Sample preparation and experiment. – By using the solid-state reaction method [18], we successfully fabricated the fluoride-arsenide polycrystalline samples AeFeAsF (Ae = Sr, Eu and Ca) and La-doped Sr$_{1-x}$La$_x$FeAsF (x = 0.0–0.4). First LaAs and SrAs (or CaAs, EuAs etc.) powders were obtained by the chemical-reaction
Fig. 1: (Color online) X-ray diffraction patterns of the samples Sr\(_{1-x}\)La\(_{x}\)FeAsF (\(x = 0.0\) and 0.20). All main peaks can be indexed by a tetragonal structure with \(a = b = 4.004\) Å and \(c = 8.971\) Å for the undoped sample SrFeAsF, \(a = b = 3.976\) Å and \(c = 8.960\) Å for the doped sample Sr\(_{0.8}\)La\(_{0.2}\)FeAsF. This indicates that the dominant phase here is Sr\(_{1-x}\)La\(_{x}\)FeAsF. Shown together are the X-ray diffraction patterns of the parent phases EuFeAsF and CaFeAsF. The asterisks mark the peaks from the impurity phase which could be given by SrF\(_2\) and LaAs.

method with La grains (purity 99.99%), Sr (or Ca, Eu etc.) pieces and As grains. Then they were mixed with FeF\(_3\) (purity 99%) and Fe powder (purity 99.99%) in the formula Ae\(_{1-x}\)La\(_x\)FeAsF, ground and pressed into a pellet shape. All the weighing, mixing and pressing procedures were performed in a glove box with a protective argon atmosphere (both H\(_2\)O and O\(_2\) are limited below 0.1 ppm). The pellet was sealed in a silica tube with 0.2 bar of Ar gas and followed by heat treatment at 950°C for 60 hours. Then it was cooled down slowly to room temperature. The resultant pellet was ground again, sealed in a silica tube for a second sintering at 1000°C for 30 hours.

The DC magnetization measurements were done with a superconducting quantum interference device (Quantum Design, SQUID, MPMS5T). The zero-field-cooled magnetization was measured by cooling the sample at zero field to 2 K, and the data were collected during the warming-up process. The field-cooled magnetization data was collected in the warming-up process after the sample was cooled down to 2 K at a finite magnetic field. The resistivity measurements were done with a physical property measurement system (Quantum Design, PPMS9T) with a four-probe technique. The current direction was changed for measuring each point in order to remove the contacting thermal power.

Results and discussion. – In the main panel of fig. 1 we present the X-ray diffraction patterns of the compound SrFeAsF and the La-doped sample Sr\(_{1-x}\)La\(_x\)FeAsF, together with the parent phases of CaFeAsF and EuFeAsF. Taking the SrFeAsF as the example, it is clear that almost all main peaks can be indexed by a tetragonal structure with \(a = b = 4.004\) Å and \(c = 8.971\) Å for the parent phase, and \(a = b = 3.976\) Å and \(c = 8.960\) Å for the doped samples. Comparing with the LaFeAsO samples, the \(a\)- or \(b\)-axes contract a bit but the \(c\)-axis lattice constant expands a lot. This is understandable since the radius of Sr\(^{2+}\) is 1.12 Å which is larger than that of La\(^{3+}\) (1.06 Å), although the radius of F\(^-\) (1.33 Å) is comparable to that of O\(^2-\) (1.32 Å). Therefore we are confident that the dominant component in our sample comes from Sr\(_{1-x}\)La\(_x\)FeAsF. There are some peaks marked by the asterisks which could be given by the impurity phase of SrF\(_2\) and LaAs. These can be easily formed during the synthesizing process and one should try to avoid the formation of these impurity phases. Data in fig. 1 clearly show that the parent phases with Sr, Ca and Eu based on SrF can be formed.

In fig. 2 we show the temperature dependence of resistivity of the undoped samples AeFeAsF. For the undoped samples, a clear resistivity anomaly is observed at about 118 K for CaFeAsF, 173 K for SrFeAsF and 153 K for EuFeAsF. Here we take the case of SrFeAsF for further discussion. Above 173 K the resistivity increases slightly with decreasing temperature, but it drops sharply below 173 K. This resistivity anomaly was found to be corresponding very well to a magnetic anomaly [15] measured by DC magnetization and was attributed to the formation of a Spin-Density-Wave order or a structural transition in REFeAsO [19,20]. By applying a magnetic field, a strong magnetoresistance was observed below 173 K (not shown here), which appeared also in the oxy-pnictide systems REFeAsO [21]. The overall behavior of resistivity mimics that of LaFeAsO, which again indicates that our samples
here are parent phases with the ZrCuSiAs structure and the FeAs layers as that in oxy-pnictides. Interestingly, it was found that the Hall coefficient $R_H$ was positive in the parent phase SrFeAsF [15], and very recently our group also proved that this is the case also for CaFeAsF and EuFeAsF. This is in contrast to the cases of the two parent compounds of the FeAs-based system known so far, namely REFeAsO and $(Ba, Sr)Fe_2As_2$. This positive Hall coefficient $R_H$ in the present fluorine-based system may suggest that one needs to dope electrons to a high level in order to induce superconductivity comparing with REFeAsO.

By doping electrons into the parent phase, we observed superconductivity in $Sr_{1-x}La_xFeAsF$. In fig. 3 we present the temperature dependence of resistivity for three samples with nominal composition $x = 0, 0.2$ and 0.4, respectively. The XRD data of the samples $x = 0$ and 0.2 were shown in fig. 1. As one can see, when electrons are doped into the system, the SDW anomaly at about 173 K is suppressed and it moves to about 60 K at the nominal composition of 0.2. Meanwhile superconductivity at about 24.4 K (onset) appears. For the doped sample $Sr_{0.6}La_{0.4}FeAsF$ a superconducting transition occurs at about 29.5 K, as indicated by the arrow where the resistivity drops about 10% of the normal-state resistivity. The state of zero resistance is achieved at about 24.6 K. It is interesting to note that the transition temperature here (29.5 K) is already much higher than the maximum $T_c = 4 \text{K}$ [17] as recently observed in $SrFe_{1-x}Co_xAsF$. This strongly suggests that doping to the sites of Sr is more efficient to get superconductors with higher $T_c$ since the FeAs-planes which are assumed for the occurrence of superconductivity remain unchanged. Occasionally, we even see superconductivity at temperatures higher than 29.5 K, but those samples exhibit quite some impurities, therefore we leave it to a future report. The resistivity of the sample with $x = 0.4$ shows a roughly linear behavior in the normal state, which looks rather similar to that in the electron-doped sample $LaFeAsO_{0.9}F_{0.1}$ [18] and is in sharp contrast to the hole-doped sample $La_{1-x}Sr_xFeAsO$ [22]. It is interesting to note that in all cases of electron- or hole-doped $ReFeAsO$, $(Ba, Sr)Fe_2As_2$, or in our present system, La-doped SrFeAsF, it seems necessary to suppress the AF order in order to induce superconductivity, this indicates that the superconductivity has a close relationship with the antiferromagnetism, which may further suggest that the AF spin fluctuation could play an important role in the pairing mechanism [23–25].

This bulk superconductivity was also proved by the magnetic measurements, as shown in fig. 4. One can see that a diamagnetic transition occurs at about 27 K, which corresponds to the middle transition temperature of the resistivity data. We believe that the superconducting transition temperature will be further improved when the synthesizing condition is further optimized. It is important to note that the superconductivity in the present sample is certainly not originated from the La-doped $SrFe_2As_2$ or the F-doped LaFeAsO. In the former case, as far as we know, no superconductivity was found in La-doped $SrFe_2As_2$. In addition, no peaks of SrFe$_2$As$_2$ can be observed from the XRD data in our present doped samples. In the latter case, one needs oxygen to form the LaFeAsO phase which is limited to be below 0.1 ppm in our case by using a glove box. Another reason to rule out this possibility is that the resistivity anomaly (the structural transition and/or SDW) occurs at 173 K in the parent phase SrFeAsF, which is much higher than that in LaFeAsO (around 150 K), but much lower than that in SrFe$_2$As$_2$ (around 205 K) [26].
**Conclusion.** – In summary, by using the combination of AeF, we fabricated the new family of fluoride-arsenide materials AeFeAsF (Ae = Sr, Eu and Ca) with the ZrCuSiAs structure. In all three cases, the parent phase exhibits a resistivity anomaly (118 K for CaFeAsF, 173 K for SrFeAsF and 153 K for EuFeAsF) which is related to the structural/SDW transition. By partially substituting Sr with La, we observed superconductivity in Sr\textsubscript{1-x}La\textsubscript{x}FeAsF (x = 0.2, 0.4). As a typical example here we show the superconductivity at 29.5 K in Sr\textsubscript{0.6}La\textsubscript{0.4}FeAsF. Using different combinations of the divalent elements (Sr, Eu, Ca, etc.) with different dopants in this fluoride-arsenide family, new superconductors are expected to be produced.

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REFERENCES

[1] Kamihara Y. et al., *J. Am. Chem. Soc.*, 130 (2008) 3296.
[2] Rotter M. et al., *Phys. Rev. Lett.*, 101 (2008) 107006.
[3] Wang X. C. et al., arXiv: 0806.4688 [cond-mat].
[4] Tapp J. H. et al., *Phys. Rev. B*, 78 (2008) (R)060505.
[5] Hsu F. C. et al., *Proc. Natl. Acad. Sci. U.S.A.*, 105 (2008) 114262.
[6] Klimczuk T. et al., arXiv: 0808.1557 [cond-mat].
[7] Ren Z. A. et al., *Chin. Phys. Lett.*, 25 (2008) 2215.
[8] Kito H., Eisaki H. and Iyo A., *J. Phys. Soc. Jpn.*, 77 (2008) 063707.
[9] Wang C. et al., *EPL*, 83 (2008) 67006.
[10] Okada H. et al., arXiv: 0810.1153 [cond-mat].
[11] Patricia L. et al., arXiv: 0807.1896 [cond-mat].
[12] Kabour H. et al., *J. Solid State Chem.*, 179 (2006) 1668.
[13] Johrendt D., Z. Naturforsch., 63b (2008) 1135.
[14] Tegel M. et al., arXiv: 0810.2120 [cond-mat].
[15] Han F. et al., *Phys. Rev. B*, 78 (2008) (R)180503.
[16] Matsuishi S. et al., *JACS*, 130 (2008) 14428.
[17] Matsuishi S. et al., arXiv: 0810.2351 [cond-mat].
[18] Zhu X. Y. et al., *Supercond. Sci. Technol.*, 21 (2008) 105001.
[19] Dong J. et al., *EPL*, 83 (2008) 27006.
[20] De la Cruz C. et al., *Nature*, 453 (2008) 899.
[21] Cheng P. et al., *Phys. Rev. B*, 78 (2008) 134508.
[22] Wen H. H. et al., *EPL*, 82 (2008) 17009.
[23] Mazin I. I. et al., *Phys. Rev. Lett.*, 101 (2008) 057003.
[24] Kuroki et al., *Phys. Rev. Lett.*, 101 (2008) 087004.
[25] Han Q., Chen Y. and Wang Z. D., *EPL*, 82 (2008) 37007.
[26] Jesche A. et al., arXiv: 0807.0632 [cond-mat].