High-\(T_c\) superconductivity induced by doping rare-earth elements into CaFeAsF

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Abstract – We have successfully synthesized the fluoride-arsenide compounds \(\text{Ca}_{1-x}\text{RE}_x\text{FeAsF}\) (RE = Nd, Pr; \(x = 0, 0.6\)). The X-ray powder diffraction confirmed that the main phases of our samples are \(\text{Ca}_{1-x}\text{RE}_x\text{FeAsF}\) with the ZrCuSiAs structure. By measuring resistivity, superconductivity was observed at 56 K in Nd-doped and 52 K in Pr-doped samples with \(x = 0.6\). Bulk superconductivity was also proved by the DC magnetization measurements in both samples. Hall effect measurements revealed hole-like charge carriers in the parent compound \(\text{CaFeAsF}\) with a clear resistivity anomaly below 118 K, while the Hall coefficient \(R_H\) in the normal state is negative for the superconducting samples \(\text{Ca}_{0.4}\text{Nd}_{0.6}\text{FeAsF}\) and \(\text{Ca}_{0.4}\text{Pr}_{0.6}\text{FeAsF}\). This indicates that the rare-earth element doping introduces electrons into \(\text{CaFeAsF}\), which induces high-temperature superconductivity.

Introduction. – Since the discovery of superconductivity in the quaternary compound \(\text{LaFeAsO}_{1-x}\text{F}_x\) with \(T_c = 26\text{K}\) [1], the quest for new high-\(T_c\) superconductors in this FeAs-based family has never ceased. Especially when replacing La with other rare-earth elements, a group of superconductors with critical temperature well exceeding 50 K were fabricated [2–4], and this has excited the whole physical community. Besides these doped \(\text{REFeAsO}\) (\(\text{RE} = \text{rare-earth elements}\)) superconductors with ZrCuSiAs-type structure (abbreviated as FeAs-1111 phase), iron-based superconductors with different structures were also synthesized, such as \(\text{Ba}_x\text{Sr}_y\text{K}_{2-x}\text{Fe}_2\text{As}_2\) (ThCr\(_2\)Si\(_2\)-type, FeAs-122) [5–7], \(\text{Li}_x\text{FeAs}\) (PbFCl-type, FeAs-111) [8–10], \(\text{FeSe}\) (PbO-type, FeAs-11) [11]. Among them the superconductors with the FeAs-1111 phase seems to have the highest superconducting transition temperature. Very recently a new series of FeAs-based compounds were successfully synthesized, namely fluoride-arsenides \(\text{AFeAsF}\) (\(\text{A} = \text{divalent metals: Ca, Sr, Eu}\)) with the ZrCuSiAs structure [12–15]. This new compound is an analogue of \(\text{REFeAsO}\), where the \((\text{REO})^+\) layer is replaced by the \((\text{AEF})^+\) layer. For \(\text{SrFeAsF}\), superconductivity could emerge by either doping cobalt directly into the FeAs-layer [16] or by partial replacement of Sr with rare-earth elements (lanthanum [15], samarium [17]). While for \(\text{CaFeAsF}\), superconductivity was also realized by doping 3d transition metals (Co and Ni) into the iron sites in the FeAs-layer with the highest \(T_c\) of about 22 K in the case of Co doping [12,18]. This relative low value of \(T_c\) could be due to the damage to the FeAs planes when substituting Fe with Co. Thus it is interesting to know whether the rare-earth elements doping could yield superconductors with higher critical temperatures, since this is the case in La-doped \(\text{SrFeAsF}\) [15], where superconductivity at about 32 K was observed. In this paper we report the discovery of high-temperature superconductivity in \(\text{Ca}_{0.4}\text{RE}_{0.6}\text{FeAsF}\) with \(T_c\) (onset) = 56 K by doping Nd and 52 K by doping Pr.

Sample preparation and experiment. – The \(\text{Ca}_{1-x}\text{RE}_x\text{FeAsF}\) samples were synthesized by the solid-state reaction method. Firstly, CaAs, NdAs and PrAs were prepared by heating calcium pieces (purity 99.99%),

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Pr pieces (purity 99.99%) and Nd pieces (purity 99.99%) with As powder (purity 99.99%), respectively, at 700 °C for 10 hours. Then stoichiometric CaAs, REAs (RE = Nd or Pr), FeF$_2$ (purity 99%) and iron powder (purity 99.99%) were mixed as the nominal composition Ca$_{1-x}$RE$_x$FeAsF ($x = 0, 0.6$), grounded and pressed into a pellet. All the processes were carried out in a glove box with argon atmosphere (both H$_2$O and O$_2$ are limited below 0.1 ppm). Finally the product was sealed in a quartz tube with 0.4 bar of high-purity Ar gas. It was then slowly heated up to and stayed at 900 °C for 20 hours and then followed by a treatment at 1050 °C for 20 hours.

The X-ray diffraction measurement was performed at room temperature using an MXP18A-HF-type diffractometer with Cu-\(K_\alpha\) radiation from 10° to 60° with steps of 0.01°. The Chemical composition was analyzed by the energy dispersive X-ray (EDX) microanalysis spectrum of a scanning electron microscope (Oxford). The analysis of X-ray powder diffraction data was done by using the software POWDER-X [19]. The DC magnetization measurements were carried out on a Quantum Design superconducting quantum interference device (SQUID) magnetometer. The resistance and Hall-effect data were collected using a six-probe technique on a Quantum Design instrument physical property measurement system (PPMS) with magnetic fields up to 9 T.

**Results and discussion.** – In fig. 1 we show the X-ray diffraction (XRD) patterns for the samples Ca$_{1-x}$RE$_x$FeAsF ($x = 0, 0.6$). One can see that the parent phase CaFeAsF is rather pure where all diffraction peaks can be indexed by the tetragonal structure with \(a = 0.3880\) nm and \(c = 0.8592\) nm. When Nd or Pr was introduced into this system some secondary phases appear, which is similar to the case in samarium-doped SrFeAsF [17]. This is understandable since CaF$_2$ is a very stable compound which can be easily formed during the reaction. The left off-stoichiometric compositions will lead to the formation of Ca$_{1-x}$RE$_x$FeAsF, Fe$_2$As and NdAs or PrAs. Therefore it would be helpful for forming the superconducting phase by blocking the formation of the CaF$_2$ phase and thus the Fe$_2$As and REAs (RE = Nd and Pr).

From fig. 1 one can see that all the main peaks of RE-doped samples could be well indexed to a ZrCuSiAs-type structure with \(a = 0.3945\) nm and \(c = 0.8594\) nm for Ca$_{0.4}$Nd$_{0.6}$FeAsF and \(a = 0.3956\) nm and \(c = 0.8594\) nm for Ca$_{0.4}$Pr$_{0.6}$FeAsF, while all the other peaks were indexed precisely to the standard XRD patterns of NdAs(PrAs), CaF$_2$ and Fe$_2$As. We all know that the radius of Pr$^{3+}$ is around 1.01 Å and Nd$^{3+}$ is 1.0 Å which are both a little larger than that of Ca$^{2+}$ (0.99 Å), so the lattice parameters may expand when rare-earth elements are doped into the lattice. Compared to CaFeAsF, the \(c\)-axis lattice constant of RE-doped sample does not increase obviously, while the \(a\)-axis lattice constant suffers a major change (it increases by about 1.6% for Nd-doped samples). A similar phenomenon was also observed in La-doped SrFeAsF [15] and Sm-doped SrFeAsF [17]. One may argue that the superconductivity here could be induced by the F-doped REFeAsO phase which might happen if some amount of oxygen leaked into the samples. This possibility can be however ruled out by the following arguments. Firstly, the weighing, mixing and pressing procedures were performed strictly in the glove box which limits the oxygen down to an undoubted low level. The dense pellet was sealed into a quartz tube quickly afterwards. There is no chance for much oxygen going into the sample. Secondly, we can also get support from the detailed analysis of the X-ray diffraction data. Taking Pr-doping as an example, the typical lattice constants of F-doped PrFeAsO with \(T_c = 52\) K were: \(a = 0.3967\) nm and \(c = 0.8561\) nm [2], which could not match any main peaks in our X-ray diffraction data. It is the same case if we compare the lattice constants of the F-doped NdFeAsO and the data from our sample Ca$_{0.4}$Nd$_{0.6}$FeAsF. Since all the other impurity peaks could be accurately indexed to the standard XRD patterns of PrAs, CaF$_2$ and Fe$_2$As (as shown in fig. 1), no traces of F-doped (Nd or Pr)FeAsO could be detected in our samples. Thirdly, the energy dispersive X-ray microanalysis (EDX) spectrum measurements were carried out on the grains of our samples. As shown in fig. 2, we could easily find the grains with the chemical composition approximately satisfying Ca$_{1-x}$RE$_x$FeAsF, and most importantly there is no oxygen in the grains. The EDX spectrums in the large area of our polycrystalline samples were done (not shown here), in which the element oxygen was also hard to be detected. From all the above aspects, we could safely exclude the possible existence of REFeAsO$_{1-x}$F$_x$.

Figure 3 shows the temperature dependence of resistivity for samples Ca$_{1-x}$RE$_x$FeAsF (RE = Nd, Pr;
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Fig. 2: (Color online) Scanning electron microscopic image and Energy dispersive X-ray microanalysis (EDX) spectrum of typical grains for Ca\(_{1-x}\)Pr\(_x\)FeAsF and Ca\(_{1-x}\)Nd\(_x\)FeAsF are shown in (a) and (b), respectively. The inset also shows the atomic ratio of the elements in the grains.

Fig. 3: (Color online) Temperature dependence of resistivity for CaFeAsF and Ca\(_{0.4}\)RE\(_{0.6}\)FeAsF (RE = Nd, Pr). The inset shows an enlarged view in the region of the superconducting transition. Here \(T_c\) (onset) is defined as the temperature at which the normal-state resistivity \(\rho\) drops by 90%.

\[ x = 0, 0.6 \]. A clear resistivity anomaly was observed at about \(T_{\text{an}} = 118\text{K}\) for the parent sample which could be attributed to the structural phase transition or an anti-ferromagnetic order. For the superconducting samples this anomaly could not be seen and a superconducting transition appears at 56 K (onset) for the Nd-doped sample and 52 K (onset) for the Pr-doped one. Here \(T_c\) (onset) is defined as the temperature at which the normal-state resistivity \(\rho\) drops by 90%. The normal-state resistivity of the superconducting samples shows a metallic behavior in a wide temperature region which is typical in these optimally doped FeAs-1111 superconductors [15].

Fig. 4: (Color online) Temperature dependence of DC magnetization for samples Ca\(_{0.4}\)Nd\(_{0.6}\)FeAsF and Ca\(_{0.4}\)Pr\(_{0.6}\)FeAsF. A DC field of 50 Oe was applied in the measurements with the zero-field-cooling and field-cooling modes.

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The bulk superconductivity of Ca\(_{0.4}\)RE\(_{0.6}\)FeAsF samples were confirmed by DC magnetization measurement, under a magnetic field of 50 Oe in zero-field-cooling and field-cooling processes. As shown in fig. 4, the onset point of the diamagnetic transition locates at about 54 K for the Nd-doped sample and 50 K for the Pr-doped one. Both samples exhibit a positive background in the normal state which may come from the impurity phase Fe\(_2\)As. It is interesting to note that a small kink appears at about 14 K in the curve of \(M\) vs. \(T\) in all superconducting samples doped with Nd. But it has never been observed in the samples with Pr-doping. Therefore we attribute this effect to the possible existence of an anti-ferromagnetic ordering of the Nd\(^{3+}\) ions because they have magnetic moments. While for Pr\(^{3+}\) ions no magnetic moment is anticipated.

To investigate the evolution of charge carriers, we conducted Hall-effect measurements on our samples. For the parent compound, as shown in fig. 5, the sign of Hall coefficient changes at \(T_{\text{an}} = 118\text{K}\). When the temperature
is above $T_{cm}$, $R_H$ is small but negative and does not change much with temperature. While below 118 K, $R_H$ becomes positive and increases quickly when temperature decreases. This phenomena could be attributed to the emergence of an anti-ferromagnetic order in the lower-temperature region. Band structure calculations showed that the Fermi surfaces of CaFeAsF are similar to that in LaFeAsO with two electron pockets in the M-point and two hole pockets in the Γ-point \[20\], the anti-ferromagnetic order removes the density of states on some Fermi pockets and may leave one of the hole pockets partially or fully ungapped thus causing the low-temperature behavior of $R_H$ \[13\]. Through partial substitution of Ca$^{2+}$ with Nd$^{3+}$ or Pr$^{3+}$, electrons were introduced into this system. As shown in fig. 5, the Hall coefficient $R_H$ was found to be negative in Cao.4RE0.6FeAsF, which confirmed that the electron-type charge carriers were doped into the system by substituting Ca partially with the trivalent rare-earth elements Nd and Pr. It should be mentioned that superconductivity was not observed in samples with low doping ($x \leq 0.2$), which could be explained by the existence of a partially or fully ungapped hole pocket in the parent phase, thus one needs to dope more electrons into the system in order to generate the superconductivity. If this is the case, it would be optimistic to induce superconductivity by a small amount of hole doping. This is just underway. We have so far made tens of samples which show superconductivity beyond 50 K in the fluoride-based systems when doping about 40–60% Nd or Pr for Ca. Further efforts are worthwhile in order to get rid of the impurity phase, especially to block the formation of CaF$_2$ during the reaction. It remains to be found out how high the superconducting transition temperature would increase if we substitute the Ca with other rare-earth elements.

**Conclusion.** – In summary, high-temperature superconductivity was observed in the compounds Cao.4(RE)0.6FeAsF (RE= Pr, Nd). The onset superconducting transition temperature is about 56 K as determined from the resistivity data in Cao.4Nd0.6FeAsF. DC magnetizations measurement confirmed the bulk superconductivity of our samples. The measurements of Hall coefficients $R_H$ reveal the evolution of charge carriers from hole-type in the parent phase CaFeAsF to electron-type in Cao.4Nd0.6FeAsF. Our results show that high-temperature superconductivity could emerge through rare-earth element doping into the (CaF)$^+$ layer in this CaFeAsF system.

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