Potassium fluoride doped LaOFeAs multi-band superconductor: Evidence of extremely high upper critical field

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Abstract – The recently discovered superconductors based on oxypnictides have rekindled the search for new non-copper based high-Tc superconductors. After the initial report by Kamihara et al. of superconductivity in (La-O/F-Fe-As)-based compounds, there have been several reports on these new superconductors but the synthesis of pure phases of these oxypnictides has remained a challenge. Here we describe a new methodology of synthesizing these oxypnictide superconductors with the commonly available potassium fluoride (KF) as a source of fluorine instead of the expensive LaF₃. This route also allows the substitution of potassium at lanthanum sites which leads to an increase in the upper critical field as would be expected for a multi-band superconductor. We also report the highest-Tc (onset) of 28.50 K and highest upper critical field at ambient pressure in the family of La-based oxypnictides.

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Introduction. – In early 2006, superconductivity was discovered in an unexpected structure by doping fluorine in an oxypnictide LaOFeP [1] with a Tc around 7 K and subsequent studies improved the Tc to 26 K in a related As-derivative (LaOFeAs) [2]. The parent compound, LaOFeAs crystallizes in a simple tetragonal structure [3] and consists of alternating LaO and FeAs layers and is an antiferromagnetic semi-metal which is reminiscent of copper oxide based high-Tc superconductors [4]. It shows a spin density wave correlation at ~150 K [5], while doping with fluorine suppresses the magnetic instability and leads to superconductivity at 26 K [2]. Recent high-field transport measurements and theoretical analysis [6] have established multi-band superconductivity in these oxypnictides. The FeAs layers provide the conducting pathway and the LaO layers act as charge reservoirs [7]. La has been replaced by other rare earths such as Nd, Pr, Gd, Ce and Sm to yield new superconductors with higher transition temperatures [8–12]. On the other hand, the transition temperature is lowered on substituting Fe by Ni [13]. The highly reactive nature of metals and metal fluorides coupled with the toxicity of pnictogens (P and As) has restricted the ability to carry out reactions with gay abandon. Hence most of the reports on the synthesis have revolved around similar lines with the use of metals and LaF₃ (Ln = rare earth) as the source of fluorine. Moreover, it is now well established that, both the upper critical field, the maximum field up to which superconductivity can be sustained and the irreversibility field that corresponds to disappearance of bulk supercurrent density, can be tuned by controlling the intra- and inter-band scattering mechanism of a multiband superconductor [14,15]. Taking both these facts into consideration, we have attempted to design a simpler process to obtain fluorine-doped oxypnictides and to achieve improved superconducting properties.

We describe a new methodology of synthesizing these oxypnictides with the commonly available KF as a source of fluorine instead of the expensive LaF₃ as used in all earlier reports [2,8–12]. The quality of the doped and undoped samples is confirmed from the sharp transitions, low room temperature resistivity, and high onset temperatures. KF doping also allows the formation of K-substituted superconducting compounds. We show that a substantial enhancement of the upper critical field can be achieved by simultaneous doping of potassium and fluorine at lanthanum and oxygen sites, respectively.
Experimental. – For the $\text{La}_{1-x}\text{K}_x\text{O}_{1-x}\text{F}_x\text{FeAs}$ ($x = 0.15$ and 0.20) synthesis, stoichiometric amounts of $\text{La}_2\text{O}_3$, FeAs, La and KF were sealed in evacuated silica ampoules (10⁻⁴ torr) and heated at 1000°C for 48 h. The powder was compacted (5 tonnes) and the disks were wrapped in Ta foils, sealed in evacuated silica ampoules and heated at 1180°C for 48 h. $\text{La}_{1.03}\text{O}_{0.9}\text{F}_{0.2}\text{FeAs}$ (K-free superconductors) was obtained by initially loading La, $\text{La}_2\text{O}_3$, FeAs, LaF₃ in a stoichiometric ratio corresponding to the composition $\text{LaO}_{0.9}\text{F}_{0.1}\text{FeAs}$. The mixture was heated at 950°C and then at 1000°C for 8 h. Additional LaF₃ was added such that the final composition corresponds to $\text{La}_{1.03}\text{O}_{0.9}\text{F}_{0.2}\text{FeAs}$. The resulting mixture was again heated as above at 1180°C for 48 h. Powder X-ray diffraction patterns of the finely ground powders were recorded with Cu-Kα radiation in the 2θ range of 10° to 70°. The lattice parameters were obtained from a least squares fit to the observed $d$ values.

The resistivity measurements were carried out ($I = 10\,\text{mA}$) using a Cryogenic 8 T Cryogen-free magnet in conjunction with a variable temperature insert (VTI). The samples were cooled in helium vapor and the temperature of the sample was measured with an accuracy of 0.05 K using a calibrated Cernox sensor wired to a Lakeshore 340 temperature controller. The external magnetic field ranging from 0 to 6 tesla was applied perpendicular to the probe current direction and the data were recorded during the warming cycle with the heating rate of 1 K/min. The inductive part of the magnetic susceptibility was measured via a tunnel diode based rf penetration depth technique [16]. The sample was kept inside an inductor that formed a part of LC circuit of an ultrastable oscillator ($\sim 2.3\,\text{MHz}$). A change in the magnetic state of the sample results in a change in the inductance of the coil and is reflected as a shift in oscillator frequency which is measured by an Agilent 53131A counter. Energy dispersive X-ray (EDAX) analysis was carried out on a Zeiss Scanning electron microscope in conjunction with a BRUKER EDX system.

Results and discussions. – Powder X-ray diffraction patterns of the nominal compositions of $\text{LaO}_{0.9}\text{F}_{0.1}\text{FeAs}$ after heating at 950 and 1000°C are shown in figs. 1a and b (fig. 1: panel (i)). After heating at 950°C (fig. 1a) unreacted $\text{La}_2\text{O}_3$ and FeAs were present along with 60% of the desired oxyquinolinate phase which increased with the heating of nearly 75% on further heating at 1000°C. On subsequent heating at 1180°C (with addition of LaF₃ resulting in nominal composition of $\text{La}_{1.03}\text{O}_{0.9}\text{F}_{0.2}\text{FeAs}$) led to an increase (~85%) in the oxyquinolinate phase (fig. 1c). It may be noted that we had around 10% of LaOF and 5% of Fe₂As as secondary phases. In all earlier reports [2,17], secondary phases like LaOF, FeAs, Fe₂As, $\text{La}_4\text{Fe}_7(\text{SiO}_4)_\text{O}$ and $\text{La}_2\text{O}_3$ have been observed. There is no report so far on the synthesis of a pure phase of $\text{La}(O/F)\text{FeAs}$.

The KF-doped compositions, $\text{La}_{1-x}\text{K}_x\text{O}_{1-x}\text{F}_x\text{FeAs}$ ($x = 0.15$ and 0.2) were also heated at 1180°C. Powder XRD studies (figs. 1d and e) show that majority of the observed reflections could be satisfactorily indexed based on the tetragonal $\text{LaOFeAs}$ (space group $P4/nmm$) phase, barring some weak reflections that were assigned to secondary phases (LaOF and Fe₂As). The refined lattice parameters ($a = 4.0270(7)$ Å and $c = 8.718(3)$ Å) for F-doped $\text{LaOFeAs}$ were smaller than those reported for pure $\text{LaOFeAs}$ [3] ($a = 4.038$ Å, $c = 8.753$ Å), as
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expected from ionic-size considerations. The first study of a F-doped compound (LaO$_{0.95}$F$_{0.05}$FeAs) showed lattice parameters of $a = 4.0355$ and $c = 8.7393$ Å [2].

In the KF-doped compositions we observed the major phase to be tetragonal with $a = 4.0293$ and $c = 8.718$ Å for $x = 0.15$ and $a = 4.039$ and $c = 8.672$ Å for the $x = 0.2$ phase. The increase in a lattice parameter (though marginal) is indicative of K doping since all reports (including ours) on fluorine-doped compositions show a decrease in both $a$ and $c$ lattice parameters compared to the undoped LaOFeAs. There is a significant variation of the $c$-parameter ($\Delta c = 0.08$ Å) among the different samples. The $a$-parameter has a much lower dependence ($\Delta a = 0.01$ Å) on either F or K substitution. This implies a considerable phase width and the presence of anisotropic bonding characteristics, which has potential implications for obtaining optimized transition temperatures in this family of superconductors.

To confirm the incorporation of K into the LaOFFeAs matrix, in fig. 1(ii) we show the EDX (energy dispersive X-ray spectroscopy) scan of the La$_{0.85}$K$_{0.15}$FeAsO$_{0.85}$F$_{0.15}$ specimen. This unambiguously establishes the presence of potassium. The presence of superconductivity in these samples indicates fluoride doping and since we do not see the presence of any potassium-containing compound in our X-ray studies it appears that potassium is incorporated in the lattice in place of La. This is also corroborated by the lattice parameter variation as discussed above. A small amount of Si is also indicated in the EDX spectra, possibly due to the formation of SiO vapor from the quartz tube employed for synthesis or from the Si detector of the microscope.

Figure 2 shows the evolution of the resistivity plots at different sintering temperatures (950–1180°C). The plots marked a and b, correspond to LaO$_{0.9}$F$_{0.1}$FeAs whose X-ray patterns are shown in figs. 1a and b, while the plot “c” corresponds to La$_{1.03}$O$_{0.9}$F$_{0.2}$FeAs (XRD pattern (c)). We find that the phase obtained by sintering at 950°C yields the non-superconducting state with characteristic decrease in resistivity at (fig. 2a) $\sim 150$ K corresponding to the spin density wave (SDW) transition [5]. On sintering at 1000°C, the high-temperature region of the resistivity plot becomes much more linear (fig. 2b) and the SDW transition disappears which is indicative of incorporation of fluorine. The superconducting transition is achieved in La$_{1.03}$O$_{0.9}$F$_{0.2}$FeAs, the sample sintered at 1180°C. The absolute value of resistivity at 300 K of the above sample is $\sim 2$ m$\Omega$cm (also confirmed in the Van der Pauw geometry) which is the smallest value reported so far [2,17].

The zero-field resistivity as a function of temperature for La$_{1.03}$O$_{0.9}$F$_{0.2}$FeAs, La$_{0.85}$K$_{0.15}$O$_{0.85}$F$_{0.15}$FeAs and La$_{0.8}$K$_{0.2}$O$_{0.4}$F$_{0.2}$FeAs is depicted in fig. 3. The insets in each panel show the resistivity over a larger temperature range and also the inductive part of susceptibility attesting the onset of bulk diamagnetic behavior. We note that the onset of superconductivity in La$_{1.03}$O$_{0.9}$F$_{0.2}$FeAs occurs at 28.5 K and 50% of the transition is achieved in a temperature interval of 0.9 K. So far this is the highest $T_c$ that has been reported in this series of compounds (La-O/F-Fe-As) [2,17,18]. The criteria used for the $T_c$ determination is the same as that used elsewhere [17] and is schematically elucidated in fig. 3a. The onset of the superconducting transition in La$_{0.85}$K$_{0.15}$O$_{0.85}$F$_{0.15}$FeAs and La$_{0.8}$K$_{0.2}$O$_{0.4}$F$_{0.2}$FeAs occurs at 26.20 K and 26.45 K, respectively (figs. 3b and c). The suppression of $T_c$ by doping of K in La sites in these oxypnictides appears to have similar origins as seen with Al and C doping in multiband MgB$_2$ [19]. The high residual resistivity (fig. 3a) ratio (RRR $= \rho_{300K}/\rho_{5K}$) for LaO$_{0.9}$F$_{0.2}$FeAs, implies that the phase is much more homogeneous as compared to those reported earlier [2]. We find a RRR value of 4.45 and K doping lowers it further suggesting enhanced impurity scattering. It is also interesting to note that while F acts as an electron donor and substitution of K in La sites leads to hole injection onto the FeAs layers, the overall transition temperature goes down marginally with potassium doping ($\sim 2$ K).

We next discuss the transport properties in the presence of an external magnetic field. The in-field resistive transitions for the samples (a) La$_{1.03}$O$_{0.9}$F$_{0.2}$FeAs and (b) La$_{0.8}$K$_{0.2}$O$_{0.4}$F$_{0.2}$FeAs are shown in fig. 4. At an applied field of 6 tesla (fig. 4a) the offset of the transition shifts by only $\sim 4$ K which is indicative of strong flux pinning. This suggests the as-grown defects to be effective pinning centers. The broadening of the in-field resistive transition is more muted as compared to that of the cuprate superconductors and augurs well from the point of view of applications. We also observe a positive magnetoresistance in La$_{1.03}$O$_{0.9}$F$_{0.2}$FeAs in the normal state which
Fig. 3: Plot of resistivity and the real part of the magnetic susceptibility. (a) La$_{1.03}$O$_{0.9}$F$_{0.2}$FeAs, (b) La$_{0.85}$K$_{0.15}$O$_{0.85}$F$_{0.15}$FeAs and (c) La$_{0.8}$K$_{0.2}$O$_{0.8}$F$_{0.2}$FeAs superconductors. The insets in each panel show the corresponding resistivity up to room temperature and rf susceptibility. The $T_c$’s are found to be (a) 28.50, (b) 26.20 and (c) 26.45, respectively.

needs further investigation. This effect is not seen in the K-doped sample. The insets of fig. 4 show the upper critical field ($H_{c2}$) and the irreversibility field ($H^*$) as a function of temperature obtained from magnetic field-dependent resistivity studies. We have used the 90% of $\rho_n$ (normal state resistivity at $T = T_c$) criteria [20] to define $H_{c2}$ and 10% criteria for the corresponding $H^*$. We must point out that the 10% criteria for the $H^*$ values are only rough estimates as this criterion would be applicable only in a high current density specimen [21]. The slope $dH_{c2}/dT$ is estimated to be $-5.3$ T/K which increases to $-6.7$ T/K with potassium doping. There is a marked curvature at low fields in the $H_{c2} vs. T$ plot (fig. 4b) which is another signature of a multi-band scattering mechanism [15]. We have therefore chosen the data between applied fields of 2 T and 6 T for the calculation of $dH_{c2}/dT$. The extrapolated $H_{c2}(0)$ values using the Werthamer-Helfand-Hohenberg
As compared to those reported earlier (33 °A [17]), the compositions. More importantly, we observe the highest is observed suggesting a definite phase width in these fluorinating agent, KF. The use of KF also allows potas-

sium doping in La-O layers that lead to optimization of silicon in La-based superconductors. This is an enormous increase in $H_{c2}(0)$ compared to the highest value of 60 T reported earlier [6,17]. Due to the polycrystalline nature of the samples, this value of the upper critical field is accompanied by a marginal decrease in $H_c$. The increase in the upper critical field is accompanied by a marginal decrease in $T_c$ with doping of “K”, which again is the hallmark of the 80 T reported earlier [6,17]. We estimate the mean-field Ginzburg-Landau coher-

ence length ($\xi_{GL} = (\Phi_0/\pi H_{c2})^{1/2}$, $\Phi_0$ being the flux quantum = 2.07 × 10^{-7} G cm²) for these oxyxnitide superconductors to be ~17 Å. These values are smaller as compared to those reported earlier (33 Å [17]).

In conclusion, we provide a novel synthesis route to prepare the lanthanum-based oxyxnitide superconductor ($T_c = 26.45$ K) using an inexpensive and easily available fluorinating agent, KF. The use of KF also allows potassium doping in La-O layers that lead to optimization of upper critical field parameters in this multiband superconductor. A variation (anisotropic) in lattice parameters is observed suggesting a definite phase width in these compositions. More importantly, we observe the highest $T_c$ of 28.50 ($\pm 0.05$ K) in La$_{0.99}$Fe$_{0.2}$As, and the highest upper critical field of 122 T (by WHH extrapolation) in La$_{0.85}$K$_{0.2}$FeAsO$_{0.8}$F$_{0.2}$ reported so far in La-based oxypnictides. The resistive broadening in the presence of external magnetic field indicates robust flux pinning in these high-field superconductors.

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