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Compositionally controlled semimetal to superconducting transition in NaF doped LaOFeAs: Enhancement in T_c due to Na-doping

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ABSTRACT

We report the synthesis of LaOFeAs based oxypnictide superconductors ($La_{1-x}Na_xO_{1-x}F_xFeAs$) using sodium fluoride as a fluorinating agent. NaF doping leads to a systematic decrease in both the **a** and **c** lattice parameters. Resistivity measurements show the onset resistivity transition temperature at 30.9 (±0.05) K and corresponding Meissner transition at 28 (±0.05) K in $La_{0.85}Na_{0.15}O_{0.85}F_{0.15}FeAs$ which is highest in LaOFeAs type superconductors synthesized at ambient pressure. Further increase of NaF content in LaOFeAs leads to suppression of T_c. The above superconductors show a negative value of the Seebeck coefficient which indicates that electrons are the dominant charge carriers.

1. Introduction

The recent discovery of superconductivity at 26 K in La(O/F)FeAs oxypnictides has attracted significant interest among the physics and chemistry community [1]. The highest transition temperature (T_c) attained in iron pnictides is reported to be 55–56 K to date which is currently the record in superconducting transition temperature among non-cuprate superconductors. These oxypnictides LnOFeAs (Ln = rare earth metals) adopt the layered tetragonal ZrCuSiAs structure (space group *P*4/*nmm*) type [2] and consist of two dimensional layers of (Ln–O) and (Fe–As) layers in which iron is tetrahedrally coordinated by four As ions while Ln ions are eight coordinated by four arsenic and four oxygen ions forming a distorted square antiprism. The Ln–O layers act as charge reservoirs while Fe–As layers act as the conducting layers [3]. The parent compound, LaOFeAs (without F doping) is a semimetal and undergoes a structural distortion from tetragonal (space group *P*4/*nmm*) to monoclinic (space group *P*112/*n*) [4] symmetry at ~155 K which accounts for anomalies at ~150 K in both resistivity and d.c. susceptibility measurements [1]. On further lowering the temperature (below 155 K), it undergoes a paramagnetic to long-range antiferromagnetic transition at 135 K. The doping of electrons in the Ln–O layers by the substitution of fluorine [1,5] at oxygen sites or by oxygen deficiency [6] suppresses the anomaly at 150 K with the emergence of superconductivity. The transition temperature enhances on substitution of smaller rare earth metals like Ce [7,8], Pr [9], Nd [10], Sm [11], Gd [12], Tb [13] and Dy [13] with a maximum T_c of 55 K in $SmO_{1-x}F_xFeAs$ [14]. Hole doping also induces superconductivity in these oxypnictides with maximum T_c at 25 K in $La_{1-x}Sr_xOFeAs$ [15]. Injection of electrons in the conducting layers (Fe–As layers) by doping cobalt at Fe sites also induces superconductivity [16,17] which is significantly different from the behavior of the cuprate superconductors where substitution of any transition metal ion in place of copper drastically lowers the T_c [18]. We have recently reported the enhancement of T_c by substitution of Sb in place of As in La(O/F)FeAs [19]. Earlier we have reported the occurrence of superconductivity in KF doped LaOFeAs where enhancement in the upper critical field was observed as compared to the F doped LaOFeAs with $T_c \sim 26.5$ K [5]. In this report we have carried out a systematic study on the effect of sodium fluoride (NaF) substitution on the structural, electrical and magnetic properties of LaOFeAs. Superconductivity is observed in these $La_{1-x}Na_xO_{1-x}F_xFeAs$ ('*x*' = 0.1, 0.15 and 0.2) oxypnictides with the highest transition temperature of 30.9 K for '*x*' = 0.15 which is the highest T_c observed so far in fluoride-doped La-based oxypnictides superconductors synthesized at ambient pressure.

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2. Experiment

The oxypnictides with nominal composition of $La_{1-x}Na_xO_{1-x}F_xFeAs$ ('x' = 0.10, 0.15 and 0.20) were synthesized by heating stoichiometric amounts of La_2O_3, NaF, La and FeAs by sealed tube method. FeAs was obtained by heating Fe and As chips in evacuated sealed silica tubes at 800 °C for 24 h. The stoichiometric amounts of La_2O_3, NaF, La and FeAs were weighed and wrapped in Ta foil and then sealed in silica ampoules under vacuum (10^{-4} torr) and heated at 800 °C for 12 h and then at 950 °C for 24 h. The resulting powder was ground and compacted (5 tonne) into disks. The disks were wrapped in Ta foil, sealed in evacuated silica ampoules and heated at 1080 °C for 48 h. All the synthetic manipulations were performed in a nitrogen-filled glove box. Powder X-ray diffraction patterns of the finely ground powders were recorded with Cu–$K\alpha$ radiation in the 2θ range of 20°–60°. The lattice parameters were obtained from a least squares fit to the observed d values.

The resistivity measurements were carried out (I = 1 mA) using a Cryogenic 8T 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 0–8 T 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 [20]. The sample was kept inside an inductor that formed a part of LC circuit of an ultrastable oscillator (~2.3 MHz). This LC part is attached to the low temperature facility to access temperature down to 1.6 K and field up to 8 T. 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 spectroscopy (EDX) was carried out with a Technai G^2 20 electron microscope operated at 200 kV which is attached with HRTEM. The specimen for TEM was prepared by dispersing the powder in benzene by ultrasonic treatment, dropping onto a porous carbon film supported on a copper grid, and then drying in vacuum. The thermoelectric power data were obtained in the bridge geometry across a 2 mm by 3 mm platelet.

3. Results and discussion

Fig. 1(i) shows the powder X-ray diffraction patterns for the nominal compositions of $La_{1-x}Na_xO_{1-x}F_xFeAs$ ('x' = 0.10(a), 0.15(b) and 0.20(c)). Majority of the observed reflections could be satisfactorily indexed on the basis of a tetragonal cell known for LaOFeAs. LaOF was present as a secondary phase. To the best of our knowledge all the reports on La(O/F)FeAs superconductors till date mention the presence of minor amounts of LaOF as a secondary phase. Both the **a** and **c**-axis lattice parameters decrease systematically with increase in NaF concentration (Fig. 1(ii)). If we assume that Na^+ substitute the La^{+3} ions and F^- substitute O^{-2} ions, this would lead to the expected decrease in lattice parameter since the size of fluoride ion is smaller than oxide ion while sodium and lanthanum ions are similar in size. The EDX spectra with the scanning transmission electron microscopy (STEM) studies was carried out on microcrystals of $La_{0.85}Na_{0.15}O_{0.85}F_{0.15}FeAs$ compound (Fig. 2) to confirm the uniform incorporation of sodium ion in the lattice. The studies show the presence of Na and F ions in addition to La, Fe, As and O with nearly same stoichiometry from different crystals are shown in Fig. 2.

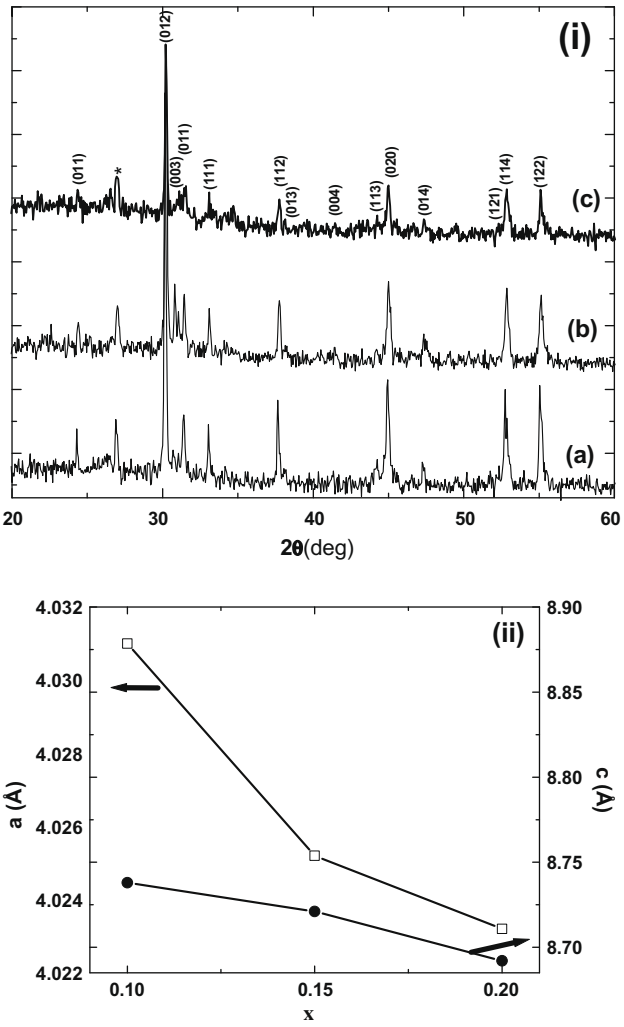

Fig. 1. (i) Powder X-ray diffraction patterns (PXRD) of (a) $La_{0.9}Na_{0.1}O_{0.9}F_{0.1}FeAs$ (b) $La_{0.85}Na_{0.15}O_{0.85}F_{0.15}$ FeAs and (c) $La_{0.8}Na_{0.2}O_{0.8}F_{0.2}FeAs$ sintered at 1080 °C. The impurity phase is LaOF (*). (ii) Variation of lattice parameters with doping for $La_{1-x}Na_xO_{1-x}F_xFeAs$.

The zero field resistivity as a function of temperature is shown in Fig. 3 as measured by standard four probe method. Fig. 3(i) shows the temperature dependence of resistivity for (a) $La_{0.9}Na_{0.1}O_{0.9}F_{0.1}FeAs$, (b) $La_{0.85}Na_{0.15}O_{0.85}F_{0.15}FeAs$ and (c) $La_{0.8}Na_{0.2}O_{0.8}F_{0.2}FeAs$. $La_{0.9}Na_{0.1}O_{0.9}F_{0.1}FeAs$ exhibits a sudden decrease of resistivity at ~150 K. Below 150 K, the resistivity continues to decrease and then becomes almost independent of temperature, below ~30 K. However the other two compounds with higher NaF content, $La_{0.85}Na_{0.15}O_{0.85}F_{0.15}FeAs$ and $La_{0.8}Na_{0.2}O_{0.8}F_{0.2}FeAs$ exhibit superconductivity. Fig. 3(ii) shows the zero field resistivity in the low temperature region for $La_{0.85}Na_{0.15}O_{0.85}F_{0.15}FeAs$. The resistivity decreases monotonously with decreasing temperature and a rapid drop was observed at 30.9 K showing onset of superconductivity. The criteria used for determination of transition temperature are same as that has been reported [21] and schematically shown in Fig. 3(ii). In our earlier report of $La_{1-x}K_xO_{1-x}F_xFeAs$ [5] a superconducting transition was observed at 26.20 K for the x = 0.15 composition which indicates that the smaller sodium ion (as compared to potassium ion) plays an important role in the enhancement of T_c.

To attest the onset of diamagnetic behavior below T_c, we show the real part of rf susceptibility in the inset of Fig. 3(ii). The bulk magnetization shows a lower T_c of ~28 K as compared to the resis-

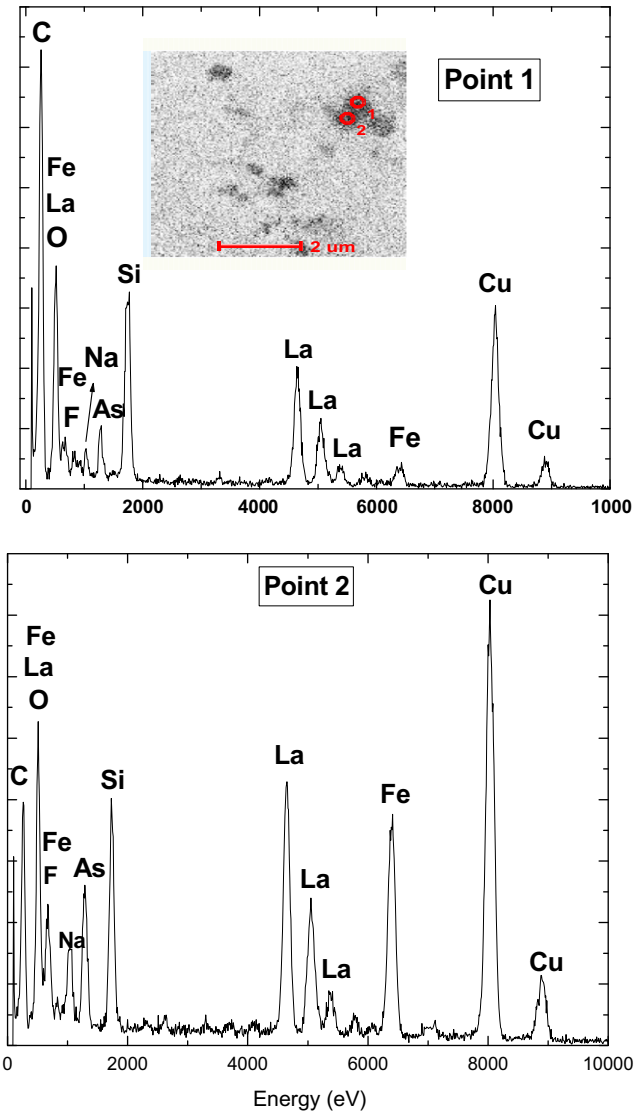

Fig. 2. EDX spectra from two microcrystals of $La_{0.85}Na_{0.15}O_{0.85}F_{0.15}FeAs$ compound. The inset shows the scanning transmission electron microscopy (STEM) image. Carbon coated copper grid is responsible for the presence of Cu and C peaks in EDX spectra while Si is due to detector of microscope.

tivity studies. Further, the broadening of the magnetic transition (inset of Fig. 3(ii)) indicates a certain degree of inhomogeneity in the polycrystalline sample. The small inhomogeneity of the sample is also clear from the value of the residual resistivity value ($RRR = \rho_{300}/\rho_{31}$) of 7.27. Nevertheless, we emphasize that the onset of superconductivity in $La_{0.85}Na_{0.15}O_{0.85}F_{0.15}FeAs$ represents the highest transition temperature in La-based oxypnictides synthesized at ambient pressure.

From the behavior of the T dependence of resistivity, one can identify two distinct regimes. We find that ρ above T_c exhibits a quadratic temperature dependence, $\rho = A + BT^2$, in the range of temperature between 45 K and 151 K which is shown in the lower inset of Fig. 3(ii). The value of B obtained from the fit is 1.91×10^{-4} mΩ cm K^{-2} and $A = 1.89$ mΩ cm. This value of B is smaller than that observed in some semi-heavy fermion compounds [22]. A systematic deviation from T^2 to T-linear behavior of resistivity is observed above 150 K. The temperature coefficient

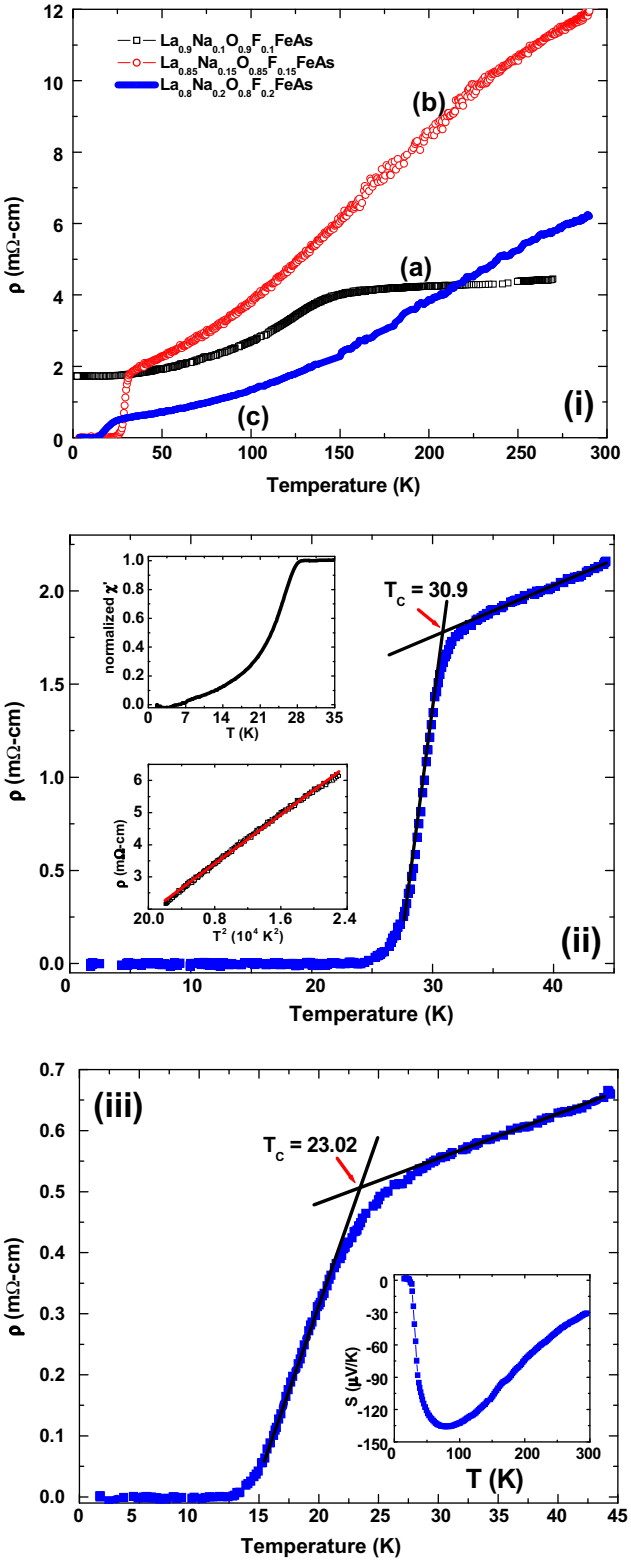

Fig. 3. (i) The temperature dependence of resistivity (ρ) up to room temperature as a function of temperature for (a) $La_{0.9}Na_{0.1}O_{0.9}F_{0.1}FeAs$ (b) $La_{0.85}Na_{0.15}O_{0.85}F_{0.15}FeAs$ (c) $La_{0.8}Na_{0.2}$ $O_{0.8}F_{0.2}FeAs$. (ii) Temperature dependence of electrical resistivity for $La_{0.85}Na_{0.15}O_{0.85}F_{0.15}$ FeAs near the superconducting transition temperature. Upper inset shows the magnetic susceptibility as a function of temperature and lower inset displays T^2 dependence of ρ for 'x' = 0.15 composition in the range 45 K $\leq T \leq$ 150 K. (iii) The electrical resistivity vs temperature for $La_{0.8}Na_{0.2}O_{0.8}F_{0.2}$-FeAs. The inset shows the temperature dependence of thermopower (S) for $La_{0.85}Na_{0.15}$ $O_{0.85}F_{0.15}FeAs$.

of ρ in the linear regime is 4.6×10^{-2} mΩ cm K^{-1}. The T^2 behavior of ρ below 150 K signifies a strong electron–electron correlation.

The temperature dependence of electrical resistivity (low temperature data) for $La_{0.8}Na_{0.2}O_{0.8}F_{0.2}FeAs$ is shown in Fig. 3(iii). For this sample too, the resistivity anomaly (at ~150 K) disappears and the resistivity drops abruptly to zero below 23 K, indicating a superconducting transition. The residual resistivity value ($RRR = \rho_{300}/\rho_{31}$) is found to be 13.79 for $La_{0.8}Na_{0.2}O_{0.8}F_{0.2}FeAs$. This value of RRR suggests good metallic conductivity and better intergrain connectivity in comparison to $La_{0.85}Na_{0.15}O_{0.85}F_{0.15}FeAs$ ($RRR = 7.27$). Further, the temperature dependence of Seebeck coefficient (S) for the 'x' = 0.15 phase is shown in inset of Fig. 3(iii). In the measured temperature range, S has a negative value. This is similar to that found in F doped LaOFeAs and provides evidence of electron doping [21]. The Seebeck coefficient varies from −34 μV/K at 300 K to a value of ~ −135 μV/K at ~80 K then decreases in magnitude as the temperature is lowered further. We note that S increases approximately linearly with T for $150\ K \leq T \leq 255\ K$ and a deviation occurs at high temperature above 255 K. This behavior is somewhat similar to the T dependence of resistivity in this temperature range (as shown in inset of Fig. 3(ii)). Below 150 K, S decreases with temperature faster than a linear rate and passes through a minimum at T_{min} and exhibits a maximum at 80 K. Using the Mott expression $S = \pi^2 k_B T\ (2eT_F)^{-1}$ and taking the value at 40 K ($S = -103$ μV/K), we calculated the Fermi energy ~ 0.014 eV. This value is smaller than that reported for $LaO_{0.89}F_{0.11}FeAs$ [21] and clearly out of the range because of strong electronic correlation. We believe that detailed Hall coefficient measurements are required to explain these subtle changes.

The upper critical field is one of the important parameters to characterize superconductivity. To get more information about H_{c2}, we have studied the temperature dependence of the resistivity under different magnetic fields which is shown in Fig. 4 for $La_{0.85}Na_{0.15}O_{0.85}F_{0.15}FeAs$. Similar measurements were also carried out for $La_{0.8}Na_{0.2}O_{0.8}F_{0.2}FeAs$. It is clear that the onset temperature shifts with magnetic field weakly, but the zero resistivity temperature shifts more rapidly to lower values. This allows one to determine the upper critical field of these materials. Taking the very onset of the transition as the upper critical field point T_c (H_{c2}) implies that almost all cooper pairs are broken at this temperature and magnetic field. By taking a criterion of 90% and 10% of normal state resistivity (ρ_n), we calculated the upper critical field H_{c2} and the irreversibility field $H*(T)$, respectively. The H–T phase diagram for each sample is shown in inset of Fig. 3. By using the Werthamer–Helfand–Hohenberg (WHH) formula [23], the zero field upper critical field $H_{c2}(0)$ can be calculated ($H_{c2}(0) = -0.693 T_c (dH_{c2}/dT)_{T=T_c}$). The slope of dH_{c2}/dT} is estimated from H–T phase diagram and is found to be −2.97 and −1.18 T/K for the 'x' = 0.15 and 'x' = 0.2 phase. Using the value of transition temperature, T_c = 30.9 K and 23 K, we find H_{c2} = 63.5 T and 19 T for $La_{0.85}Na_{0.15}O_{0.85}F_{0.15}FeAs$ and $La_{0.8}Na_{0.2}O_{0.8}F_{0.2}FeAs$, respectively. These values are smaller than the reported H_{c2} value of La(O/F)FeAs and (La/K)(O/F)FeAs [5]. So the incorporation of sodium ion at La site enhances the T_c but on the other hand suppresses the H_{c2} value as compared to KF doped LaOFeAs [5]. This indicates the role of sodium ion on the superconducting properties of La(O/F)FeAs. Using the value of H_{c2} (0) we can also calculate the mean field Ginzburg–Landau coherence length by the formula ($\xi_{GL} = (\Phi_0/2\pi H_{c2})^{1/2}$). By taking $\Phi_0 = 2.07 \times 10^{-7}$ G cm^2 and the calculated H_{c2} values, we estimate a coherence length of ~23 Å and 42 Å for samples with 'x' = 0.15 and 'x' = 0.2, respectively. These values are higher than that reported for La(O/F)FeAs [5].

In conclusion, we have successfully synthesized a new series of oxypnictides superconductors with nominal compositions of $La_{1-x}Na_xO_{1-x}F_xFeAs$ with 'x' = 0.15 and 0.20 using sodium fluoride as a fluorinating agent at relatively low temperature (1080 °C) by sealed tube method. By substituting NaF in LaOFeAs, a systematic change of superconducting transition temperature is observed and the maximum T_c is found to be 30.9 K. This is the highest transition temperature in Lanthanum based oxypnictides containing fluoride ions and synthesized at ambient pressure. With increasing temperature (T), the resistivity above T_c crosses over from a T^2 dependence due to electron–electron interaction to a linear T dependence. The thermoelectric power measurement indicates that the dominant carriers are electrons. From magnetoresistance studies the value of the upper critical field (H_{c2}) is estimated to be 64 T corresponding to a coherence length (ξ_{GL}) of ~23 Å for 'x' = 0.15 composition. The increase of T_c with sodium ion while a decrease with potassium ions [5] clearly indicate the role of dopant size (lattice) in controlling on the superconducting transition temperature.

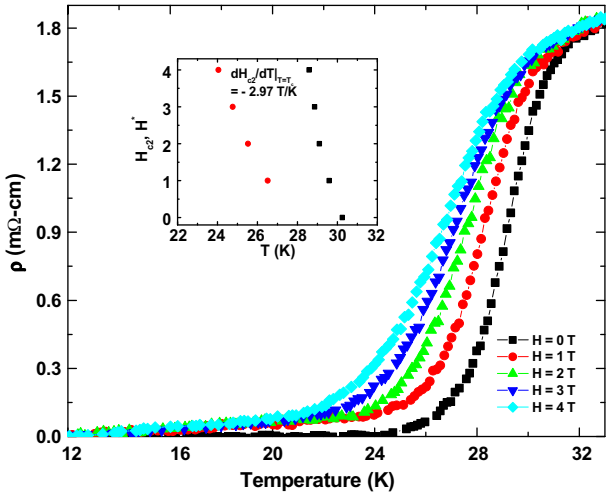

Fig. 4. Temperature dependence of the electrical resistivity of $La_{0.85}Na_{0.15}O_{0.85}F_{0.15}FeAs$ under different magnetic fields. Inset shows the temperature dependence of estimated upper critical field (■) and irreversibility field (●).

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