

Superconductivity at 31.3 K in Yb-doped La(O/F)FeAs superconductors

J PRAKASH^a, S J SINGH^b, S PATNAIK^b and A K GANGULI^{a,*}

^aDepartment of Chemistry, Indian Institute of Technology, New Delhi 110 016

^bSchool of Physical Sciences, Jawaharlal Nehru University, New Delhi 110 067

e-mail: ashok@chemistry.iitd.ernet.in

Abstract. The effect of ytterbium substitution at the lanthanum site on the superconducting properties of $\text{La}_{1-x}\text{Yb}_x\text{O}_{0.8}\text{F}_{0.2}\text{FeAs}$ ($x = 0.10, 0.20$ and 0.30) oxypnictides has been investigated. Powder X-ray diffraction studies show the presence of Yb_2O_3 and LaOF as secondary phases. The superconducting transition temperature (T_c) of 31.3 (± 0.05) K has been observed in $x = 0.1$ composition which is the maximum T_c so far in the La(O/F)FeAs superconductor family at ambient pressure. Further increase in x leads to suppression and broadening of superconducting transition. The resistive transition curves under different magnetic fields were investigated, leading to determination of upper critical field $H_{c2}(T)$ of this new superconductor. The value of H_{c2} at zero temperature is estimated to be about 46 T corresponding to coherence length ~ 27 Å.

Keywords. Oxypnictides; superconductivity; upper critical field.

1. Introduction

The recent discovery of superconductivity in Ln(O/F)FeAs oxypnictides with critical temperature (T_c) higher than McMillian limit of 39 K (theoretical maximum T_c according to BCS theory) has generated great excitement.¹ These oxypnictides LnOFeAs ($\text{Ln} =$ rare earth metals) crystallize in the layered tetragonal ZrCuSiAs structure ('filled' PbFCl) type² with the space group $P4/nmm$ and consist of two-dimensional layers of (Ln-O) and anti- PbO or anti-fluorite-type (Fe-As) layers in which iron is tetrahedrally coordinated by four As ions while Ln ions are coordinated by four arsenic and four oxygen ions forming a distorted square antiprism. The Ln-O layers act as charge reservoir while Fe-As layers act as conducting layers.³ The parent compound, LaOFeAs is an antiferromagnetic semi-metal and shows anomalies at ~ 150 K in both resistivity and d.c. magnetic susceptibility⁴ due to structural transition from tetragonal space group ($P4/nmm$) to a monoclinic space group ($P112/n$).⁵ Electron doping by substituting fluorine⁶ at oxygen sites or by oxygen deficiency⁷ leads to superconductivity and the T_c enhances on substitution of smaller rare earth metals like Ce,⁸ Pr,⁹ Nd,¹⁰ Sm,¹¹ Gd,¹¹ Tb¹² and Dy¹² with maximum T_c of 55 K in $\text{SmO}_{1-x}\text{F}_x\text{FeAs}$.¹³ Hole dop-

ing in LnOFeAs also leads to superconductivity with maximum T_c at 25 K in $\text{La}_{1-x}\text{Sr}_x\text{OFeAs}$.¹⁴ There are also reports of superconductivity induced by Co-doping at Fe sites^{15,16} in LnOFeAs oxypnictides. We have recently reported the enhancement of T_c by substitution of Sb in place of As in La(O/F)FeAs superconductor.¹⁷ In this paper, we have studied the effect of Yb substitution at La site in $\text{La}_{1-x}\text{Yb}_x\text{O}_{0.8}\text{F}_{0.2}\text{FeAs}$ ($x = 0.10, 0.20$ and 0.30).

2. Experimental

The oxypnictides with nominal compositions of $\text{La}_{1-x}\text{Yb}_x\text{O}_{0.8}\text{F}_{0.2}\text{FeAs}$ ($x = 0.10, 0.20$ and 0.30) were synthesized by heating stoichiometric amounts of La_2O_3 , Yb_2O_3 , LaF_3 , 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 , Yb_2O_3 , LaF_3 , La and FeAs were weighed in a N_2 filled glove box and sealed in silica ampoules under vacuum (10^{-4} torr) and heated at 950°C for 24 h. The resulting powder was ground and compacted (5 tonnes) into disks. The disks were wrapped in Ta foil, sealed in evacuated silica ampoules and heated at 1180°C for 48 h. Powder X-ray diffraction patterns of the finely ground powders were recorded with $\text{Cu-K}\alpha$ radiation in the 2θ range of 20° to 60°.

*For correspondence

The lattice parameters were obtained from a least squares fit to the observed d values.

The resistivity measurements were carried out 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 to 5 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 using a tunnel diode based r.f. penetration depth technique.¹⁸ The sample was kept inside an inductor that formed a part of LC circuit of an ultrastable oscillator (~ 2.3 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.

3. Results and discussion

Figure 1 shows the Powder X-ray diffraction patterns (PXRD) of $\text{La}_{1-x}\text{Yb}_x\text{O}_{0.8}\text{F}_{0.2}\text{FeAs}$ ($x = 0.10, 0.20$ and 0.30). Majority of the observed reflections

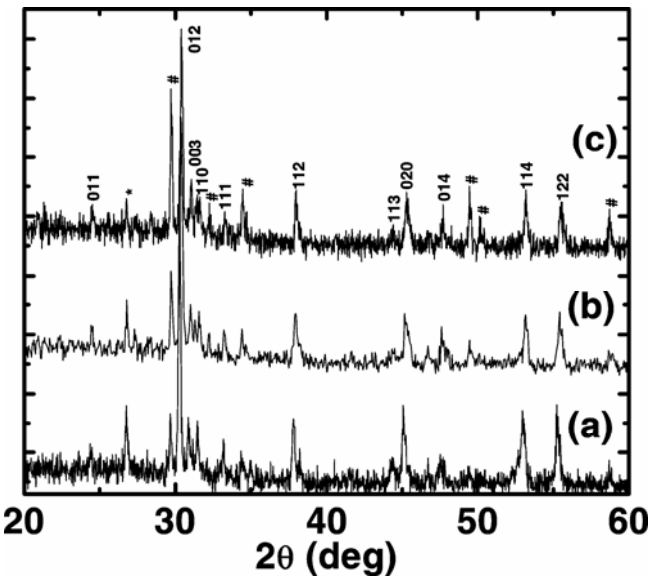


Figure 1. (i) Powder X-ray diffraction patterns (XRD) of (a) $\text{La}_{0.9}\text{Yb}_{0.1}\text{O}_{0.8}\text{F}_{0.2}\text{FeAs}$, (b) $\text{La}_{0.8}\text{Yb}_{0.2}\text{O}_{0.8}\text{F}_{0.2}\text{FeAs}$ and (c) $\text{La}_{0.7}\text{Yb}_{0.3}\text{O}_{0.8}\text{F}_{0.2}\text{FeAs}$ sintered at 1180°C . The impurity phases are LaOF (*) and Yb_2O_3 (#).

could be satisfactorily indexed on the basis of tetragonal ZrCuSiAs structure with LaOF and Yb_2O_3 as secondary phases. To the best of our knowledge all the reports of La(O/F)FeAs superconductors show the presence of LaOF as a secondary phase. The refined lattice parameters ($a = 4.0202(6)$ Å, $c = 8.703(2)$ Å for $x = 0.1$; $a = 4.0112(5)$ Å, $c = 8.673(2)$ Å for $x = 0.2$; $a = 4.005(1)$ Å, $c = 8.680(5)$ Å for $x = 0.3$) were found to be smaller than the parent LaOFeAs (ref. 2) ($a = 4.038$ Å, $c = 8.753$ Å) which suggests the substitution of Yb in the La sites. The amount of Yb_2O_3 (secondary phase) increases with increase in x .

The zero field resistivity as a function of temperature for the nominal compositions $\text{La}_{1-x}\text{Yb}_x\text{O}_{0.8}\text{F}_{0.2}\text{FeAs}$ ($x = 0.10, 0.20$ and 0.30) are shown in figure 2 (the lower inset shows the resistivity over a larger range of temperature) measured by standard four probe method. The resistivity decreases monotonously with decreasing temperature and the onset of superconducting transition occurs at 31.3, 26.3 and 23.2 K for $x = 0.1$, $x = 0.2$ and $x = 0.3$ compositions respectively. For $x = 0.2$ and $x = 0.3$, the transition is rather broad and the T_c values are approximate. The criteria used for the determination of T_c are the same as that used earlier¹⁹ and schematically shown in figure 2. The residual resistivity value ($\text{RRR} = \rho_{300}/\rho_{31.5}$) of 10.6, 12.2 and 13.7 for samples (a), (b) and (c) respectively suggests good metallic conductivity and reasonable normal-state connectivity. The inductive part of the r.f. magnetic susceptibility attesting the onset of bulk diamagnetic state is shown in upper inset of figures 2(a) and (b).

The T_c of 31.3 K observed for $\text{La}_{0.9}\text{Yb}_{0.1}\text{O}_{0.8}\text{F}_{0.2}\text{FeAs}$ synthesized at ambient pressure is the highest known in the La(O/F)FeAs family of superconducting oxypnictides. This enhancement in T_c indicates that small amount of ytterbium is substituted at the La sites. The smaller size of Yb as compared to lanthanum will lead to subtle changes in the bandwidth and this probably enhances the superconducting transition temperature. However, in the compositions with higher ytterbium concentration, the superconducting transition temperature decreases and the transition broadens which suggests the compositional dependence of T_c .

We have also studied the temperature dependence of the resistivity under varying magnetic fields which is shown in figures 3(a), (b) and (c) for samples (a), (b) and (c) respectively. From figure 3 it is clear that the T_c (onset) shifts weakly with magnetic

field, but the zero resistivity temperature shifts much more rapidly to lower temperatures. Taking the onset of the transition as the upper critical field,

point T_{c2} (H_{c2}) corresponds to a situation where all cooper pairs are broken at this temperature and magnetic field. Using a criterion of 90% and 10% of

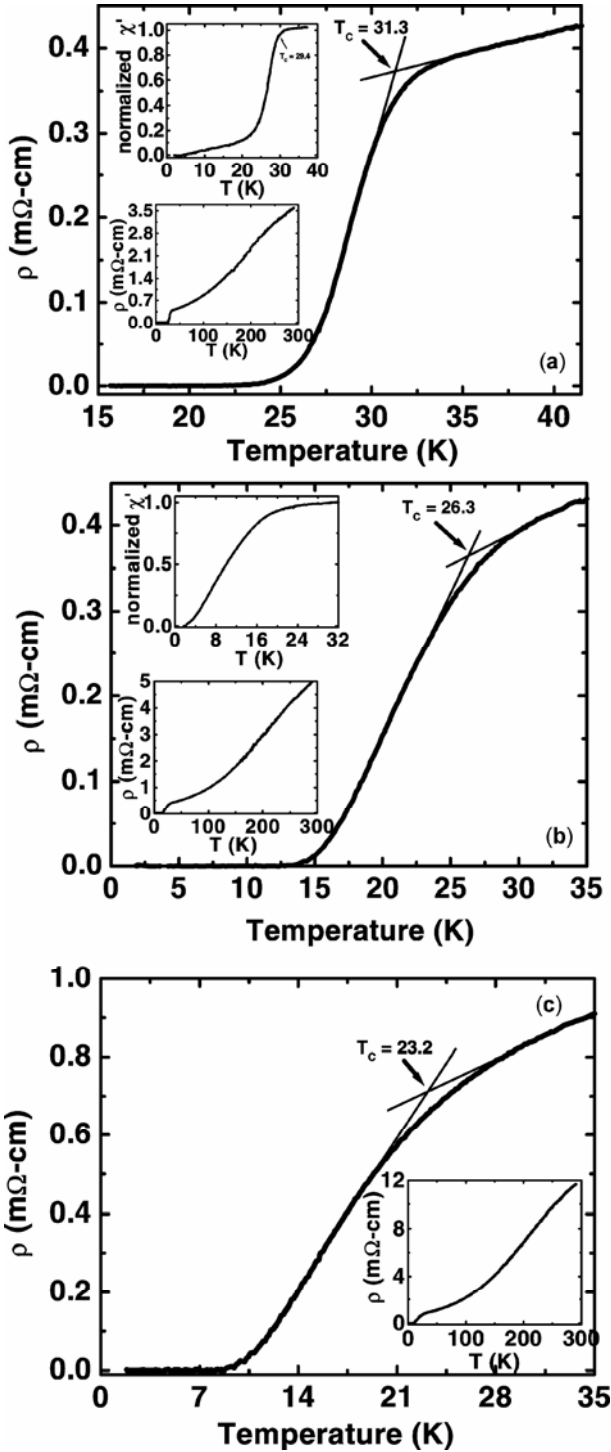


Figure 2. The temperature dependence of resistivity (ρ) as a function of temperature for (a) $\text{La}_{0.9}\text{Yb}_{0.1}\text{O}_{0.8}\text{F}_{0.2}\text{FeAs}$, (b) $\text{La}_{0.8}\text{Yb}_{0.2}\text{O}_{0.8}\text{F}_{0.2}\text{FeAs}$ and (c) $\text{La}_{0.7}\text{Yb}_{0.3}\text{O}_{0.8}\text{F}_{0.2}\text{FeAs}$. Upper inset shows the magnetic susceptibility as a function of temperature and lower inset shows the resistivity up to room temperature.

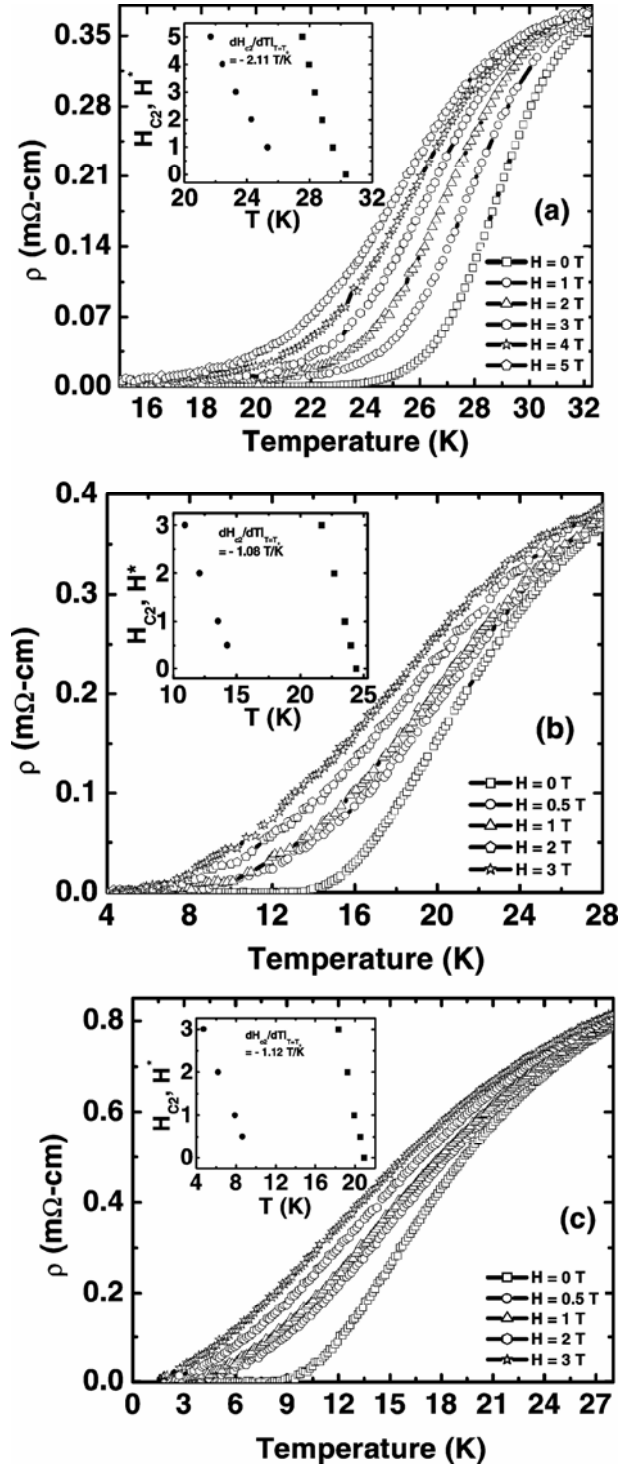


Figure 3. Temperature dependence of the electrical resistivity of (a) $\text{La}_{0.9}\text{Yb}_{0.1}\text{O}_{0.8}\text{F}_{0.2}\text{FeAs}$, (b) $\text{La}_{0.8}\text{Yb}_{0.2}\text{O}_{0.8}\text{F}_{0.2}\text{FeAs}$ and (c) $\text{La}_{0.7}\text{Yb}_{0.3}\text{O}_{0.8}\text{F}_{0.2}\text{FeAs}$ under varying magnetic fields. Inset shows the temperature dependence of upper critical field (\blacksquare) and irreversibility field (\bullet) as a function of temperature.

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 figure 3(a), (b) and (c). By using the Werthamer–Helfand–Hohenberg (WHH) formula,²⁰ the zero field upper critical field $H_{c2}(0)$ can be calculated:

$$H_{c2}(0) = -0.693T_c (dH_{c2}/dT)_{T=T_c}.$$

The slope of dH_{c2}/dT estimated from phase diagram (shown in inset) is -2.11 , -1.08 and -1.11 T/K for sample (a), (b) and (c) respectively. Using the value of the transition temperature (T_c) of 31.3 K, 26.3 K and 23.2 K, we find $H_{c2} = 46$ T, 20 T and 18 T for $\text{La}_{0.9}\text{Yb}_{0.1}\text{O}_{0.8}\text{F}_{0.2}\text{FeAs}$, $\text{La}_{0.8}\text{Yb}_{0.2}\text{O}_{0.8}\text{F}_{0.2}\text{FeAs}$ and $\text{La}_{0.7}\text{Yb}_{0.3}\text{O}_{0.8}\text{F}_{0.2}\text{FeAs}$ respectively. These values are smaller than the reported H_{c2} value of $\text{La}(\text{O}/\text{F})\text{FeAs}$.⁶ Using the value of $H_{c2}(0)$ we can also calculate the mean field Ginzberg–Landau coherence length ($\xi_{\text{GL}} = (\phi/2\pi H_{c2})^{1/2}$). Using $\phi_0 = 2.07 \times 10^{-7}$ G cm² and the H_{c2} value, we obtain a coherence length of ~ 27 Å for sample $\text{La}_{0.9}\text{Yb}_{0.1}\text{O}_{0.8}\text{F}_{0.2}\text{FeAs}$ (with highest T_c). This value is higher than that reported for $\text{La}(\text{O}/\text{F})\text{FeAs}$.⁶

4. Conclusions

We have successfully synthesized new members of the La-based oxypnictide series with nominal compositions of $\text{La}_{0.9}\text{Yb}_{0.1}\text{O}_{0.8}\text{F}_{0.2}\text{FeAs}$, $\text{La}_{0.8}\text{Yb}_{0.2}\text{O}_{0.8}\text{F}_{0.2}\text{FeAs}$ and $\text{La}_{0.7}\text{Yb}_{0.3}\text{O}_{0.8}\text{F}_{0.2}\text{FeAs}$. These new superconducting oxypnictides were obtained by substituting Yb ions in $\text{LaO}_{0.8}\text{F}_{0.2}\text{FeAs}$. The transition temperature of 31.3 K obtained for $x = 0.1$ composition is the highest reported in La-based oxypnictides at ambient pressure. From magneto-resistance studies, we obtained an upper critical field of 46 T corresponding to a coherence length ~ 27 Å in the above composition.

Acknowledgements

A K G and S P thank the Department of Science and Technology (DST), Govt. of India for financial support. J P and S J S thank Council of Scientific and

Industrial Research (CSIR) and University Grants Commission (UGC), Govt. of India, respectively for fellowships.

References

1. Chen X H, Wu T, Wu G, Liu R H, Chen H and Fang D F 2008 *Nature* **453** 76
2. Zimmer B I, Jeitschko W, Albering J H, Glaum R and Reehuis M 1995 *J. Alloys. Compd.* **229** 238
3. Takahashi H, Igawa K, Arii K, Kamihara Y, Hirano M and Hosono H 2008 *Nature* **453** 376
4. Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 *J. Amer. Chem. Soc.* **130** 3296
5. Cruz C R, Huang Q, Lynn J W, Li J, Ratcliff W II, Zarestky J L, Mook H A, Chen G F, Luo J L, Wang N L and Dai P 2008 *Nature* **453** 899
6. Prakash J, Singh S J, Patnaik S and Ganguli 2008 *Europhys. Lett.* **84** 57003
7. Ren Z-A, Che G-C, Dong X-L, Yang J, Lu W, Yi W, Shen X-L, Li Z-C, Sun L-L, Zhou F and Zhao Z-X 2008 *Europhys. Lett.* **83** 17002
8. Chen G F, Li Z, Wu D, Li G, Hu W Z, Dong J, Zheng P, Luo J L and Wang N L 2008 *Phys. Rev. Lett.* **100** 247002
9. Ren Z-A, Yang J, Lu W, Yi W, Che G-C, Dong X-L, Sun L-L and Zhao Z-X 2008 *Mater. Res. Innovations* **12** 1
10. Ren Z-A, Yang J, Lu W, Yi W, Shen X-L, Li Z-C, Che G-C, Dong X-L, Sun L-L, Zhou F and Zhao Z-X 2008 *Europhys. Lett.* **82** 57002
11. Yang J, Li Z-C, Lu W, Yi W, Shen X-L, Ren Z-A, Che G-C, Dong X-L, Sun L-L, Zhou F and Zhao Z-X 2008 *Supercond. Sci. Technol.* **21** 08200
12. Bos J W G, Penny G B S, Rodgers J A, Sokolov D A, Huxley A D and Attfield J P 2008 *Chem. Commun.* **31** 3634
13. Ren Z-A, Wei L, Jie Y, Wei Y, Li S X, Cai L Z, Can C G, Li D X, Ling S L, Fang Z and Xian Z Z 2008 *Chin. Phys. Lett.* **25** 2215
14. Wen H-H, Mu G, Fang L, Yang H and Zhu X 2008 *Europhys. Lett.* **82** 17009
15. Prakash J, Singh S J, Patnaik S and Ganguli A K 2009 *Solid State Commun.* **149** 181
16. Qi Y, Gao Z, Wang L, Wang D, Zhang X and Ma Y 2008 *Supercond. Sci. Technol.* **21** 1150
17. Singh S J, Prakash J, Patnaik S and Ganguli A K 2009 *Supercond. Sci. Technol.* **22** 045017
18. Patnaik S, Singh K J and Budhani R C 1999 *Rev. Sci. Instrum.* **70** 1494
19. Sefat A S, Mcquire M A, Sales B C, Jin R, Howe J Y and Mandrus D 2008 *Phys. Rev.* **77** 174503
20. Werthamer N R, Helfand E and Hohenberg P C 1966 *Phys. Rev.* **147** 295