Electrical and Magnetic Behaviour of PrFeAsO$_{0.8}$F$_{0.2}$ Superconductor

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1 Introduction

Interest of superconductivity in the scientific community was rejuvenated with the happening of a breakthrough in February 2008 when superconductivity at 26 K was realised in a F-doped LaFeAsO compound by a Japanese group led by Professor Hosono [1]. With great efforts of experimentalists within a short span, six different families of iron-based superconductors were realised [2]. All of these families have a common structural feature, i.e., existence of a tetrahedral Fe-pnictogen (As/P) or Fe-chalcogen(Se/Te) layer in which iron atoms are sitting on the corner of square plane and pnictogen/chalcogen sitting above and below this plane. This tetrahedral layer is separated from the rare-earth and oxygen/fluorine layer. The Fe-chalcogen/pnictogen planes are the main building blocks responsible for appearance of superconductivity in these iron-based superconductors, which are sandwiched by other layers. Other layers, on the other hand, play a vital role in determining the electronic properties of superconducting block either by donating charges or creating internal pressure to the FeAs/FeSe layers. Interestingly, these quaternary oxy-pnictides-type compounds have been synthesised way back by a German group with ZrCuSiAs-type structure and a general formula REOMPn, where RE = La, Ce, Pr, Nd, Sm, Eu, and Gd, etc., M = Mn, Fe, Co, and Ni, etc. and Pn = P and As [3]. Some of
these compounds show superconductivity at low temperature, forming a new family of superconductors other than cuprates with a layered structure [4]. Pristine REFeAsO (RE = rare earth) compounds are non-superconducting and do exhibit a structural change from tetragonal to orthorhombic at around 150 K followed by an AFM-like ordering of Fe spins, and finally RE magnetic ordering at low temperature [5–11]. The REFeAsO show superconductivity of up to 55 K (RE = Sm) by O−2 site F−1 doping [12, 13]. Theoricians studied the role of electron doping and point out that 3d orbitals of Fe give the Fermi surface a hole at Γ-point and an electron at M-point in a reduced Brillouin zone [14, 15].

Spin density wave state (SDW) or anti-ferromagnetic ordering is due to nesting of the Γ-point and M-point in the undoped pristine REFeAsO compounds. Electron doping suppresses SDW and superconductivity appears because of the dynamical spin fluctuations caused by nesting [16–20].

At low temperature, magnetic moments on the rare-earth sites are ordered anti-ferro-magnetically, which is obviously missing in the case of nonmagnetic La [5–9]. Pr in PrFeAsO showed the highest \( T^\text{Pr}_N = 12 \) K [5], which is attributed to sensitive interaction between Fe and Pr moments as revealed by Mossbauer [21] and μSR [22] studies. The anomalous ordering of Pr (\( T^\text{Pr}_N = 12 \) K) in PrFeAsO has been studied in detail by specific heat (Cp) and negative thermal expansion (NTE) experiments [23–25]. Keeping in view the anomalous ordering of Pr in PrFeAsO [5, 21–25], here we study the high field electrical and magnetic properties of the pure and fluorine doped PrFeAsO and PrFeAsO\(_{0.8}\)F\(_{0.2}\) samples, which are prepared by the single step method.

### 2 Experimental

We took Pr ingots and the powder of As, PrF\(_3\), Fe, and Fe\(_2\)O\(_3\) in their stoichiometry ratio to prepare the polycrystalline samples with nominal composition PrFeAsO and PrFeAsO\(_{0.8}\)F\(_{0.2}\). The ingots and the powders are weighed and grinded in a controlled atmosphere of Glove Box. The grinded sample is palletized and sealed in an evacuated quartz tube prior to sintering. The sample is sintered at 550 °C for 8 hours, followed by 950 °C for 12 hours, and finally at 1150 °C for 33 hours. The detailed procedure of this single step preparation had been reported by us in [26]. The phase purity and the room temperature structural parameters were determined by the powder X-ray diffraction pattern using CuK\(_\alpha\) radiation on the Desktop Rigaku-Miniflex II diffractometer. Rietveld analysis is performed with the help of the Fullprof programme. The resistivity and magnetization measurements were carried on a Quantum Design Physical Property (PPMS) measurement system.
Table 2  Reitveld refined parameters for PrFeAsO and PrFeAsO$_{0.8}$F$_{0.2}$

| Sample         | $a^0$ (Å) | $c^0$ (Å) | Volume (Å$^3$) | $Z_{Pr}$ | $Z_{As}$ | Rwp | $\chi^2$ |
|----------------|-----------|-----------|---------------|----------|----------|-----|---------|
| PrFeAsO        | 3.981(4)  | 8.593(1)  | 136.22        | 0.13755  | 0.65645  | 4.80| 2.59    |
| PrFeAsO$_{0.8}$F$_{0.2}$ | 3.972(4)  | 8.572(3)  | 135.27        | 0.15556  | 0.65406  | 6.19| 3.78    |

Fig. 2  (a) The temperature dependence of resistivity for the PrFeAsO and PrFeAsO$_{0.8}$F$_{0.2}$ samples synthesised by the single step method. Inset, shows the $d\rho/dT$ versus $T$ curve for PrFeAsO sample in extended low temperature regime. (b) Magneto-resistivity behaviour $\rho(T)$ $H$ for PrFeAsO$_{0.8}$F$_{0.2}$ sample under applied fields of up to 12 Tesla. (c) Upper critical field $H_{c2}$ versus $T$ for plots PrFeAsO$_{0.8}$F$_{0.2}$ superconductor at 90 %, 50 %, and 10 % normal resistivity criteria. (d) Dependence of upper critical field $H_{c2}(T)$ with temperature for PrFeAsO$_{0.8}$F$_{0.2}$ sample using Ginzburg–Landau (GL) equation for 90 %, 50 %, and 10 % drop of the normal state resistivity.

PrFeAsO has the highest RE ordering temperature of around 12 K. The resistivity of superconducting PrFeAsO$_{0.8}$F$_{0.2}$ sample decreases with temperature, and an onset of superconducting transition occurred at around 47 K followed by superconductivity with $T_c$ $(\rho = 0)$ at 38 K. The transition is rather broad accompanied with a long tail near $\rho = 0$ state. C.R. Rotundu et al. [32] investigated a detailed phase diagram of PrFeAsO$_{1-x}$F$_x$. The structural and anti-ferromagnetism suppression starts with 8 % fluorine doping, and optimum superconductivity is achieved at 15 % to 22 % doping of fluorine. The $T_c$ of PrFeAsO$_{0.8}$F$_{0.2}$, in our case, is slightly lower as compared to others [28, 32] and could be due to a slightly lesser amount of fluorine in the sample, which is difficult to identify exactly. The ionic size of rare earth also plays pivotal role in deciding the transition temperature ($T_c$) [27, 28], in the case of NdFeAsO$_{0.8}$F$_{0.2}$ and SmFeAsO$_{0.8}$F$_{0.2}$ the $T_c$ is found to be 48 K and 53 K, respectively [33, 34]. Figure 2(b) shows the temperature dependence of electrical resistivity with respect to varying magnetic field, i.e., $\rho(T)$ vs. $H$ under 0.1 to 12 Tesla.
applied magnetic field. The resistance drops to almost zero at \( \sim 38 \) K in zero field. Under an applied magnetic field though the \( T_{c}^{\text{onset}} \) remains nearly invariant, the \( T_{c}(\rho = 0) \) is decreased to lower temperatures. This means the superconducting transition width becomes wider with applied field. Here, we define upper critical field \( H_{c2} \) as transition temperature \( T_{c}(H) \), which is equal to 90 \% of the normal state value \( (\rho_N) \) for the applied field \( H \). The \( T_{c}(H) \) values are 46.16 K and 43.91 K at 0 and 12 Tesla, respectively. The calculated value of \( dH_{c2}/dT \) is around 4 Tesla/K. The transition width \( \Delta T_{c} = T_{c} \text{ (90 \%)} - T_{c} \text{ (10 \%)} \) are 7.64 K and 14.7 K for 0 and 12 Tesla, respectively. The broadening between \( T_{c}^{\text{onset}} \) and \( T_{c}(\rho = 0) \) with applied field is considered to be due to the weak links between grains and magnetic flux flow through the vortices [8]. Figure 2(c) shows the temperature dependence of \( H_{c2} \) for 90 \%, 50 \%, and 10 \% of \( \rho_N \). In all cases, an obvious sharp increase in \( H_{c2} \) is noticed with decreasing temperature along with a weak upward curvature near transition \( (T_{c}) \) region. Similar observations have been reported in other ReFeAsO\(_{1-x}\)F\(_{x}\) compounds [34–36]. Figure 2(d) shows the variation of upper critical field, which is determined by using different criteria of \( H_{c2} \) at \( \rho = 90 \%, 50 \%, \) and 10 \% of \( \rho_N \), here \( \rho_N \) is normal resistivity. The \( H_{c2} \) variation with temperature is depicted in Fig. 2(d), we used Ginzburg–Landau (GL) equation to find the \( H_{c2}(0) \) value.

\[
H_{c2}(T) = H_{c2}(0)(1 - t^2)/(1 + t^2),
\]

where \( t = T/T_{c} \) is the reduced temperature [37]. The estimated values for our sample at \( H_{c2} \) (90 \%), \( H_{c2} \) (50 \%), and \( H_{c2} \) (10 \%) are 182 Tesla, 73 Tesla and 41.6 Tesla, respectively.

Figure 3(a) shows the iso-thermal magnetization \( M(H) \) plots for PrFeAsO\(_{0.8}\)F\(_{0.2}\) at 5, 10, 20, and 30 K. The lower critical field \( (H_{c1}) \) is determined as the deviation from the linear MH behaviour of the curve. The lower critical field \( (H_{c1}) \) values are observed at around 120, 220, and 340 Oe at 30, 20, and 10 K, respectively. Figure 3(b) shows the iso-thermal magnetization loops of the studied compound PrFeAsO\(_{0.8}\)F\(_{0.2}\) at 5 and 50 K in higher applied fields of up to 7 kOe. The critical current density \( (J_c) \) of the PrFeAsO\(_{0.8}\)F\(_{0.2}\) sample has been estimated by using Bean's critical state model. For a bar shape sample, the magnetic critical current density can be calculated using the relation \( J_c = 20\Delta M/\pi(a/3b) \). Here, \( \Delta M \) is the width of hysteresis loop and \( a \) and \( b \) are dimensions of the sample, with \( a < b \) and the magnetic field direction is perpendicular to the plane. The critical current density roughly estimated from the observed \( M(H) \) curve is order of \( \sim 10^3 \) A/cm\(^2\) at 5 K. The critical current density of a polycrystalline samples are far less than the estimated values of the single crystal. The critical current density for a single crystal of PrFeAsO\(_{0.7}\) \( (T_c = 35 \text{ K}) \), is reported \( 2.9 \times 10^5 \) A/cm\(^2\) by Kashiwaya et al. [38]. Figure 4 shows the DC magnetic susceptibility \( (\chi) \) in zero field cooled (ZFC) and field cooled (FC) situations in the temperature range 5 to 50 K under an applied field of 10 Oe. At around 42 K, a diamagnetic onset transition appears, which shows bulk nature of superconductivity in studied PrFeAsO\(_{0.8}\)F\(_{0.2}\) sample. The estimated value of volume fraction \( \sim 7 \% \) in Meissner state and the shielding
fraction is around 16%. Because of the impurities, pinning defects and the magnetic contribution of the PrFe ions determination of exact value of volume fraction is not possible.

In conclusion, we have synthesised pristine and superconducting sample of PrFeAsO with fluorine doping by an easy single step method. The ground state of the pristine compound (PrFeAsO) exhibited magnetic ordering of Fe moments at around 150 K, followed by the unusual antiferromagnetic ordering of Pr at 12 K. Both these transitions are missing in the case of F doped superconducting PrFeAsO$_{0.8}$F$_{0.2}$ sample. The PrFeAsO$_{0.8}$F$_{0.2}$ sample exhibited bulk superconductivity at below 42 K. The sample is characterised for its magnetic and electrical behaviour under 12 Tesla field. The upper critical field is estimated to be ~182 Tesla. The critical current density ($J_c$) value as calculated by applying Bean’s critical model, which is of the order of $\sim 10^3$ A/cm$^2$.

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