

# Inter-comparison of electric and magnetic behaviour of superconducting quaternary oxy-pnictide compounds

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**Abstract.** Three different oxy-pnictides 'REFeAsO' compounds are prepared by simple and easy solid state single step method. Structural analysis is carried with the help of the X-ray technique and confirms that the obtained samples are phase pure and crystallized in tetragonal P4/nmm structure. Superconductivity is introduced by partial replacement of oxygen by Fluorine in NdFeAsO<sub>0.8</sub>F<sub>0.2</sub>, SmFeAsO<sub>0.8</sub>F<sub>0.2</sub> and PrFeAsO<sub>0.8</sub>F<sub>0.2</sub>, with highest T<sub>c</sub>(48K) in NdFeAsO<sub>0.8</sub>F<sub>0.2</sub>. SmFeAsO<sub>0.8</sub>F<sub>0.2</sub> compound shows the highest upper critical field (H<sub>c2</sub>) ~ 377 Tesla, estimated using Ginzburg Landau, (GL). Critical current density doesn't change significantly. The measured MR (magneto resistance) for PrFeAsO is 21.5%, whereas it is 16% for SmFeAsO. Here, we report in brief an inter-comparison of various properties like electric and magnetic transport, magneto-resistance for these synthesized oxy-pnictide compounds.

## 1. Introduction

In year 2008, *Y. Kamihara* reported superconductivity in LaFeAsOF at 26K[1]. Within few months, T<sub>c</sub> increased up to 43K, with the application of high pressure (4GPa) [2]. Though, strong local magnetic moment of iron are considered harmful for superconductivity, in contrast to that few superconductors are found having iron as non magnetic for example ThFe<sub>3</sub> (T<sub>c</sub> = 1.8K)[3], U<sub>6</sub>Fe (T<sub>c</sub> = 3.9K)[4], Lu<sub>2</sub>Fe<sub>3</sub>Si<sub>5</sub> (T<sub>c</sub> = 6.1K)[5], all these show transition at low temperatures. Under very high pressure (20GPa) iron it-self shows superconductivity at 1.8K[6]. On replacing the Rare earth elements (RE) with lower radii like (RE= Ce, Pr, Sm, Nd etc) the highest reported T<sub>c</sub> is 52-56K[7, 8]. Six different Iron superconductors have been discovered and they are known by the convention 11, 111, 1111, 122, 21311/42622 and 32522\*. Superconductivity may be seen in all of them except in 32522\* and the highest is seen in 1111 (REFeAsO). Structurally, iron atoms are tetrahedrally coordinated with either pnictogen (P or As, group 15 elements) or chalcogen (S, Se and Te, group 16 elements) anions, form planer layers which are sandwiched by other layers of alkali, alkali earth or rare earth metal and oxygen/fluorine. These layers either donate charges or make the internal pressure to the FeAs layers such that they influence the electronic properties and are considered to be responsible for superconductivity, similar to the Cu-O planes in Cuprates. Here the discussion is restricted to 1111, REFeAsPnO (RE =Rare earth, Pn = P & As) family only. ReFeAsO compounds are crystallized in tetragonal ZrCuSiAs type structure, with a space group P4/nmm[9]. Mostly, undoped/pristine 1111 type compounds are non superconductors and show a structural phase transition T<sub>s</sub> (tetrahedral to orthorhombic) around 120 -140K followed by an anti-ferromagnetic ordering (SDW) below 150K due to



Fermi surface nesting[10]. Low temperature Neutron Diffraction studies suggested that bond angle in the tetrahedra and the height of the pnictide and chalcogenides are the indicator of the superconductivity transition[11, 12]. The SDW may be suppressed by either electron or hole doping and superconductivity may be introduced, e.g., in REFeAsO<sub>1-x</sub>F<sub>x</sub> and REFeAsO<sub>1-y</sub>. The dynamical spin fluctuations caused by Fermi surface nesting is considered to be responsible for superconductivity[10]. Here, we report comparative studies of synthesized iron pnictide in its pristine form and in their superconducting state, with different rare earth (*4f*) elements. Superconductivity has been introduced by partially substitution of Fluorine at oxygen[13]. Structural analysis has been carried out with XRD measurements on the prepared samples. Different characterization like resistivity  $\rho(T)$ , resistivity under varying magnetic field [ $\rho(T)H$ ] and magnetization vs field has been carried out for synthesized samples to study their electrical and magnetic behaviour. Standard model “Ginzburg Landau (GL)” was used to estimate the upper critical field. The MR for ground state of Pr and Sm has been compared in this communication.

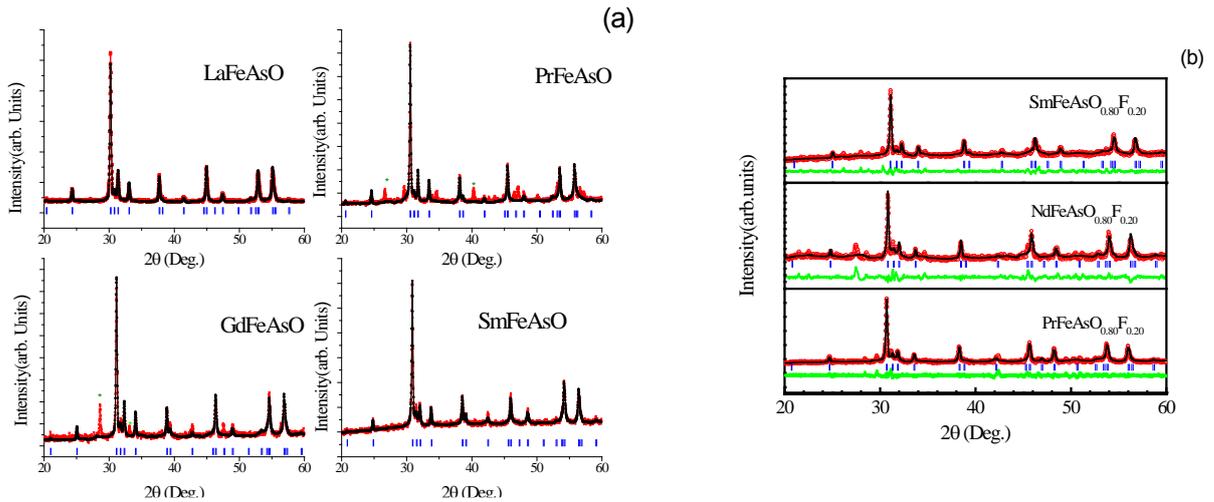
## 2. Experimental Details

Polycrystalline REFeAsO bulk samples are prepared by easy single step solid-state reaction method. The sample preparation has been carried out in the controlled atmosphere of Argon in a Glove box (MBRAUN Lab Star make, with less than 1 ppm O<sub>2</sub> and moisture). Rare earth elements like RE = Sm, Gd, La, Pr & Nd (ingots), transition metal viz., iron, iron-oxide, Rare-earth fluorides and pnictogen (metalloids) like arsenic with high purity (~99.9%) are taken as starting material, weighed and ground in a proper stoichiometric ratio. The prepared samples are pelletized in rectangular shape by applying uniaxial force of 100-120 kg/cm<sup>2</sup> in a hydraulic press. These pellets were then sealed in evacuated quartz tube and finally sintered in high temperature furnace. A good quality furnace is used for sintering the quartz sealed ampoules. The furnace is programmed for 12 hours at 550<sup>o</sup>C, 12 hours at 850<sup>o</sup>C and finally for 33 hours at 1150<sup>o</sup>C followed by slow ramp rate[14]. A slow sintering at 550<sup>o</sup>C gives good results and reduce the chances of arsenic sublimation. Re-sintering is done at 1150<sup>o</sup>C for 12 hours to obtain a denser and harder pellet, so the transport measurements like resistivity and specific heat can be performed. The room temperature structural parameters and phase purity are determined by the powder X-ray diffraction pattern using CuK $\alpha$  radiation on the Desktop Rigaku-Miniflex II diffractometer. Reitveld analysis is performed with the help of the Fullprof program. The resistivity and magnetization measurements are carried on a Quantum Design Physical Property (PPMS) measurement system.

## 3. Result and Discussion

### 3.1 Structural analysis

The room temperature XRD pattern along with their Rietveld refinements for undoped REFeAsO, with RE =Pr, Gd, Sm and La samples are shown in figure 1(a) and the plots for superconducting samples of REFeAsO<sub>0.8</sub>F<sub>0.2</sub> (RE= Sm, Pr and Nd) are shown in figure 1(b). The studied samples are crystallized in tetragonal ZrCuSAs structure with space group P4/nmm. All the permitted diffraction planes of these samples are marked with blue vertical lines under the observed and fitted patterns. Few minor impurity peaks have been observed, are marked with ‘\*’, which are mainly from un-reacted FeAs and REAS. Rietveld refined structural parameters for different REFeAsO with space group P4/nmm are shown in table 1 and the lattice parameters are shown in table 2. The obtained values of lattice parameters are in comparable to values of other reports [7, 15]. Shrinking of lattice parameters has been witnessed on the partial substitution of Fluorine at Oxygen site for the superconducting samples.



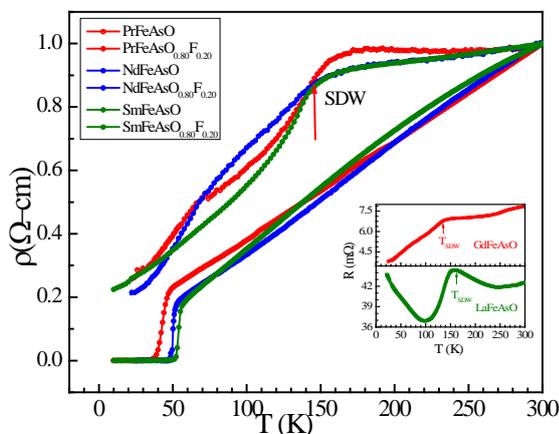
**Figure 1.** Rietveld refinement for room temperature XRD pattern of various REFeAsO (RE=La, Pr, Gd and Sm) Few REFeAsO<sub>0.8</sub>F<sub>0.2</sub> (RE= Sm, Nd & Pr)

**Table 1.** Rietveld refined parameters for REFeAsO, Space group *P4/nmm*.

Atom	Site	x	y	z (La)	z (Pr)	z (Gd)	z (Sm)	z (Nd)
RE	2c	0.25	0.25	0.142(4)	0.137(2)	0.137(4)	0.137(4)	0.138(1)
Fe	2b	0.75	0.25	0.5	0.5	0.5	0.5	0.5
As	2c	0.25	0.25	0.650(1)	0.6549(1)	0.657(1)	0.662(4)	0.657
O	2a	0.75	0.25	0	0	0	0	0

**Table 2.** Lattice parameters and cell volume of REFeAsO & REFeAsO<sub>0.8</sub>F<sub>0.2</sub>

Sample	a (Å)	c (Å)	Volume (Å <sup>3</sup> )
LaFeAsO	4.030 (3)	8.729(7)	141.47(2)
PrFeAsO	3.981(4)	8.593(1)	136.22(1)
GdFeAsO	3.915 (3)	8.454 (2)	129.60(3)
NdFeAsO	3.969(1)	8.596(3)	135.42 (2)
SmFeAsO	3.937(2)	8.492(1)	131.64(1)
PrFeAsO <sub>0.8</sub> F <sub>0.2</sub>	3.972(4)	8.572(3)	135.27(2)
NdFeAsO <sub>0.8</sub> F <sub>0.2</sub>	3.956(6)	8.539(2)	133.64(2)
SmFeAsO <sub>0.8</sub> F <sub>0.2</sub>	3.926(2)	8.460(4)	130.42(4)



**Figure 2.** Room temperature resistivity versus temperature ( $\rho$ -T) plot for REFeAsO (RE=Pr, Nd and Sm) and REFeAsO<sub>0.8</sub>F<sub>0.2</sub> (RE=Pr, Nd and Sm) compounds, inset shows RT of ground state of LaFeAsO and GdFeAsO samples.

### 3.2 Resistivity analysis

The resistivity versus temperature ( $\rho$ -T) plot for various REFeAsO (RE = Sm, Pr & Nd) are shown in figure 2. The resistivity plots show less metallic behavior from ambient temperature to down to 140- 150K and later it drops abruptly. This is attributed to phase change anomaly in the compound at around 140-150 K

[16] due to the spin density wave (SDW) transition of the system around this temperature[17]. The shape of  $\rho(T)$  curves for all the samples are similar except for LaFeAsO, as shown in the inset in figure 1, similar pattern has been observed by J. Dong et. al [16]. These pristine REFeAsO samples are non-superconducting, which can be suppressed via induction of electrons or holes by fluorine doping or by creating oxygen deficiency and hence superconductivity can be introduced[1, 2, 18]. The superconductivity transition of REFeAsO<sub>0.8</sub>F<sub>0.2</sub> (RE=Pr, Nd and Sm) samples are shown in figure 2 [19-21]. The superconductivity  $T_c$  (onset) for NdFeAsO<sub>0.8</sub>F<sub>0.2</sub>, SmFeAsO<sub>0.8</sub>F<sub>0.2</sub> and PrFeAsO<sub>0.8</sub>F<sub>0.2</sub> are around 51K, 51.7K and 47K respectively. Finally  $T_c(\rho=0)$ , the superconductivity was established at of 48K, 44.8K and at 38K for NdFeAsO<sub>0.8</sub>F<sub>0.2</sub>, SmFeAsO<sub>0.8</sub>F<sub>0.2</sub> and PrFeAsO<sub>0.8</sub>F<sub>0.2</sub> respectively. All of these compounds show metallic behaviour before superconductivity onset. NdFeAsO<sub>0.8</sub>F<sub>0.2</sub> is having the highest  $T_c$  among all three prepared superconducting samples. Since amount of Fluorine in oxy-pnictide compounds plays vital role in introducing superconducting transition, variation in Fluorine amount changes transition temperature. Here, the  $T_c$  of NdFeAsO<sub>0.8</sub>F<sub>0.2</sub> and PrFeAsO<sub>0.8</sub>F<sub>0.2</sub> are slightly lesser in comparison to some of the reports[8].

### 3.3 Magnetization measurements

The temperature dependence of electrical resistivity  $\rho(T)$  Vs H with respect to varying magnetic field from 0 Tesla to 13 T for REFeAsO<sub>0.8</sub>F<sub>0.2</sub> (RE=Pr, Nd and Sm) samples are shown in figure 3. The onset shifts to lower temperature with the applied magnetic field (H) for all the measured samples. The transition width becomes wider with applied field on decreasing temperature, exhibiting a characteristic of type II superconductor. Here the transition temperature  $T_c(H)$  is defined as temperature, which satisfies the condition that  $\rho(T_c, H)$  equals to 90% of the normal-state value ( $\rho_N$ ) for applied field H. The upper critical field  $H_{c2}(0)$  value is determine with the help of Ginzburg Landau (GL) theory. GL theory not only determine the  $H_{c2}$  value at zero Kelvin [ $H_{c2}(0)$ ], but also determines the temperature dependence of critical field for the whole temperature range.

The GL equation is:

$$H_{c2}(T)=H_{c2}(0)\left[\frac{(1-t^2)}{(1+t^2)}\right]$$

Where,  $t = T/T_c$  is the reduced temperature and  $H_{c2}(0)$  is the upper critical field at zero temperature. The estimated  $H_{c2}(90\%)$  value for NdFeAsO<sub>0.8</sub>F<sub>0.2</sub>, SmFeAsO<sub>0.8</sub>F<sub>0.2</sub> and PrFeAsO<sub>0.8</sub>F<sub>0.2</sub> are 345 T, 377T and 182T respectively at 0K, the details has been reported in [19, 21, 22]. Lower critical field ( $H_{c1}$ ) for NdFeAsO<sub>0.8</sub>F<sub>0.2</sub>, SmFeAsO<sub>0.8</sub>F<sub>0.2</sub> and PrFeAsO<sub>0.8</sub>F<sub>0.2</sub> is estimated and found highest for NdFeAsO<sub>0.8</sub>F<sub>0.2</sub> (1000 Oe at 5 K).

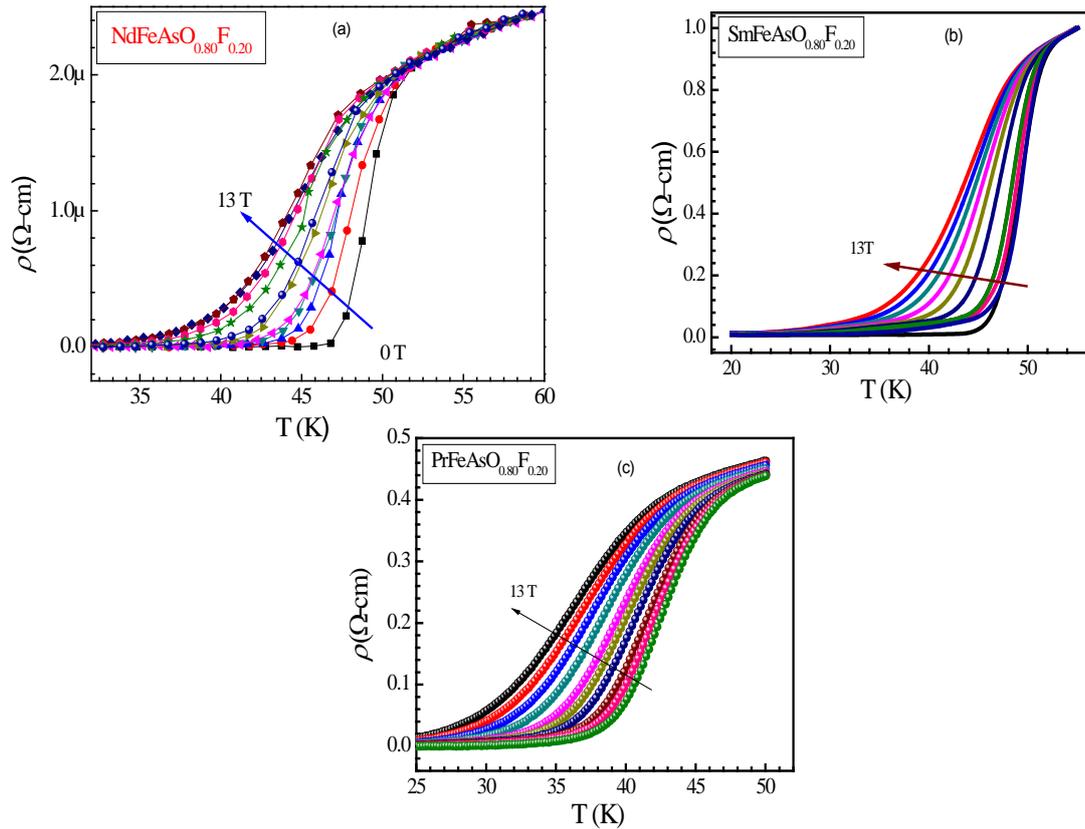
### 3.4 Magneto resistance measurement

Since MR is a very powerful tool to investigate the electronic scattering process and information about the Fermi surface, we have carried out MR measurements with varying magnetic field (0 to 14 Tesla) on these samples.

The mathematical formulation of MR is

$$MR(H) = \Delta\rho/\rho(0)$$

Where,  $\Delta\rho = \rho(H) - \rho(0)$ ,  $\rho(H)$  is the resistivity in applied field H and  $\rho_0$  is the resistivity at zero field.



**Figure 3.** The temperature dependence of the electrical resistance  $\rho(T)H$  of superconducting samples  $\text{NdFeAsO}_{0.80}\text{F}_{0.20}$ ,  $\text{SmFeAsO}_{0.80}\text{F}_{0.20}$  and  $\text{PrFeAsO}_{0.80}\text{F}_{0.20}$  sample in applied magnetic field from 0 to 13 Tesla.

The dependence of MR% with field for  $\text{SmFeAsO}$  and  $\text{PrFeAsO}$  at various temperatures below 200K are shown in figures 4(a) and 4(b).  $\text{PrFeAsO}$  samples exhibit a linear MR phenomena among the other  $\text{REFeAsO}$  family and the ground state properties are different for this compound [22, 23]. The change in MR is not even 2% in the temperature range 200-150K, up to an applied magnetic field of 14 Tesla for  $\text{SmFeAsO}$  and  $\text{PrFeAsO}$ . After the structural transition and consequent anti-ferromagnetic SDW ordering below 150 K, the MR% increases rapidly and reaches 16% for  $\text{SmFeAsO}$  and 21.5% for  $\text{PrFeAsO}$  figure 4(a & b) at 2.5K under applied field of 14 Tesla [24]. A non linear variation of MR in  $\text{SmFeAsO}$  has been observed with field. Also the linearity of MR increases with decreasing temperature, but at lower fields it remains non-linear even at 2.5 K. The observed variation of MR on H was found linear in H of strength ( $|H| \geq 3.5$  Tesla), but changed from a linear to a quadratic relation ( $\text{MR} \propto H^2$ ) in lower fields ( $|H| \leq 1$  Tesla) at 2.5 K, as shown in figure 4(a). The non-linearity of  $\text{PrFeAsO}$  disappears below 40K and a linear behaviour for MR has been reported with field [24]. Similar behaviour has been seen for prepared  $\text{PrFeAsO}$  sample with maximum MR change of 21.5% at 5 K and 14Tesla. The MR versus H curve develops a weak negligible curvature in the low- field region, which indicates a crossover to a quadratic behaviour as  $H \rightarrow 0$ . The dependence of MR on H is linear in field strength ( $|H| \leq 1.5$  Tesla) and changed from a linear to quadratic ( $\text{MR} \propto H^2$ ) for lower H values ( $|H| \leq 5$  Tesla) at 20 K as shown in figure 4(b).

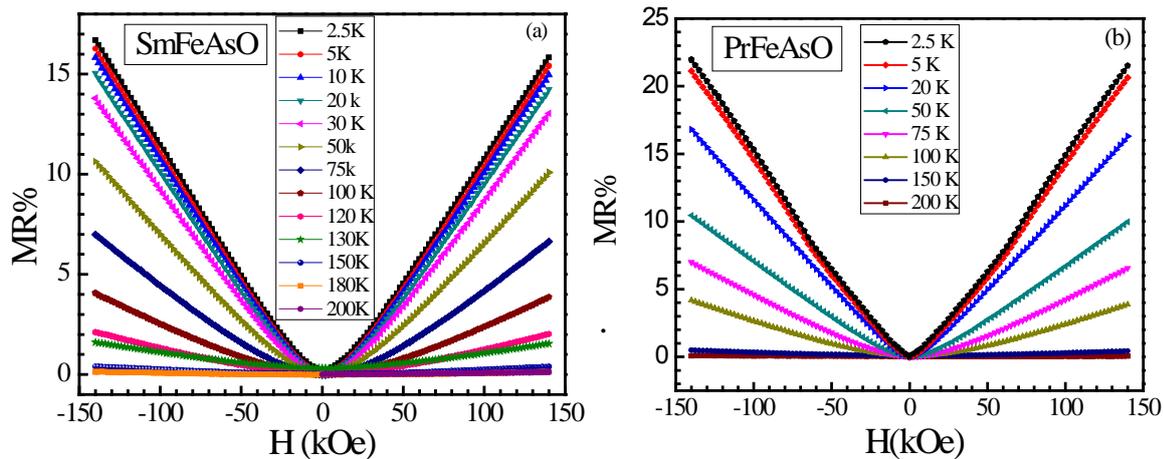


Figure 4 (a & b) Variation of MR with magnetic field (0-140 kOe) at different temperature in (a) SmFeAsO (b) PrFeAsO samples

#### 4. Conclusion

In summary, pristine samples of oxypnictides, REFeAsO (RE= La, Pr, Gd, Nd & Sm) are synthesized and superconductivity was introduced by partial substitution of Fluorine at oxygen site. Systematic studies are carried out to know their structural, electrical and magnetic properties. In iron-pnictides two competing states exist, i.e., anti-ferromagnetic ordering and superconducting state. The synthesized pristine, LaFeAsO, GdFeAsO, NdFeAsO, SmFeAsO and PrFeAsO compounds crystallized in tetragonal P4/nmm structure. Superconductivity in NdFeAsO<sub>0.8</sub>F<sub>0.2</sub>, SmFeAsO<sub>0.8</sub>F<sub>0.2</sub> and PrFeAsO<sub>0.8</sub>F<sub>0.2</sub> is introduced by partial replacement of oxygen by Fluorine. The T<sub>c</sub> of NdFeAsO<sub>0.8</sub>F<sub>0.2</sub> is observed at 48K which is highest among these synthesized systems. SmFeAsO<sub>0.8</sub>F<sub>0.2</sub> compound shows the highest upper critical field (H<sub>c2</sub>) ~ 377 Tesla, estimated by GL equation among the three systems. No significant change has been observed in values of critical current density for all of the three systems. The measured MR (magneto resistance) for PrFeAsO is 21.5%, whereas it is 16% for SmFeAsO. In the oxypnictide compounds, the bond angles and bond distance between Fe-As atoms play a crucial role in suppression of anti-ferromagnetism and introducing superconductivity, which may be done by either by Fluorine doping or by applying high pressure.

#### Acknowledge

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