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# Chemical pressure effect in $CeFeAs_{1-x}P_xO_{0.95}F_{0.05}$

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## ABSTRACT

We investigate the chemical pressure effect due to P doping in the CeFeAs<sub>1-x</sub>P<sub>x</sub>O<sub>0.95</sub>F<sub>0.05</sub> ( $0 \le x \le 0.4$ ) system. The compound CeFeAsO<sub>0.95</sub>F<sub>0.05</sub> without P doping is on the boundary between antiferromagnet (AFM) and superconductor. The AFM order of Ce<sup>3+</sup> local moments causes a significant reentrance behavior in both resistivity and magnetic susceptibility. Upon P doping, *T<sub>c</sub>* increases and reaches a maximum of 21.3 K at *x*=0.15, and then it is suppressed to lower temperatures. Meanwhile, the AFM order of Ce<sup>3+</sup> ions remains nearly the same in the whole doping range ( $0 \le x \le 0.4$ ). Our experimental results suggest a competition between superconductivity and Kondo effect in the Ce 1111 system.

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# 1. Introduction

Since the recent discovery of 26 K superconductivity (SC) in layered rare earth oxy-pnictide compound LaFeAsO<sub>1-x</sub> $F_x$  [1], great efforts have been made in searching new high  $T_c$  superconductors [2–6]. In all these rare earth oxy-pnictides, there is a structural phase transition below about 150 K, accompanied with a stripetype antiferromagnetic (AFM) ordering associated with Fe<sup>2+</sup> ions [7–9]. Chemical doping of  $F^-$  on  $O^{2-}$  site suppresses both structure transition and AFM order by introducing electron-type charge carriers to the FeAs-layers, resulting in the appearance of SC. On the other hand, the studies on the effect of high pressure on superconductivity [10–13], have revealed the doping (e.g. the F content) dependence of pressure effect, as summarized in Ref. [14]. Namely, the high pressure will enhance  $T_c$  for the underdoped samples, and affect  $T_c$  only slightly for the optimally  $F^-$  doped samples, but suppress  $T_c$  for overdoped samples. This doping dependence of pressure effect was also seen in 122 system, and is very different from the case of high  $T_c$  cuprate superconductors [15].

Chemical pressure induced by P doping on As site has been proved to be effective to induce SC in pnictide parent compounds, both in 1111 [16] and 122 [17–19] systems. We have previously systematically studied the phase diagram of CeFeAs<sub>1-x</sub>P<sub>x</sub>O [20], where two quantum critical points were proposed [21], corresponding to the disappearance of Fe<sup>2+</sup> AFM order at  $x_{c_1} = 0.37$  and of Ce<sup>3+</sup> magnetism at  $x_{c_2} = 0.92$ , respectively, and furthermore, a third critical point standing for the evolution of AFM to ferromagnetic (FM) ordering of Ce<sup>3+</sup> at  $x_{c_3}$  coincides to be close to  $x_{c_1}$ . However, no SC was observed down to 2 K in the whole

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P doping range for this system. We proposed a scenario of competition between Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction and Kondo scale, and the absence of SC was attributed to the strong Ce-4*f* spin fluctuation near the two critical points.

In this paper, we report the investigation of chemical pressure effect on CeFeAsO<sub>0.95</sub>F<sub>0.05</sub> by P doping on As site. Our results point to an on-the-boundary superconductor of CeFeAsO<sub>0.95</sub>F<sub>0.05</sub> with  $T_c$ =13.3 K, accompanied by a reentrance caused by AFM order of Ce<sup>3+</sup> ions at  $T_N$ =2.8 K. Furthermore, the chemical pressure dependence of  $T_c$  is also dome-like, i.e.,  $T_c$  is firstly enhanced with increasing P doping, reaches a maximum of 21.3 K at x =0.15, and finally decreases. However, the AFM order temperature ( $T_N$ ) corresponding to Ce<sup>3+</sup> ions does not change very much with P content x. Combined with previous reports [20,11,13], our results provide the evidence for the competition between SC and Kondo effect.

#### 2. Experimental

We have synthesized a series of CeFeAs<sub>1-x</sub>P<sub>x</sub>O<sub>0.95</sub>F<sub>0.05</sub> (x=0, 0.05, 0.1, 0.15, 0.2, 0.3, and 0.4) polycrystalline samples by solid state reaction method. Ce, Fe, As, P, CeF<sub>3</sub> and CeO<sub>2</sub> of high purity ( $\geq$  99.95%) were used as the starting materials. Firstly, CeAs (or CeP) was presynthesized by reacting Ce discs and As (or P) powders at 1323 K for 72 h. FeAs (or FeP) was presynthesized by reacting Fe and As (or P) powders at 973 K for 20 h. Secondly, powders of CeAs, CeP, CeO<sub>2</sub>, CeF<sub>3</sub>, FeAs and FeP were weighted according to the stoichiometric ratio, throughly ground, and pressed into a pellet under a pressure of 600 MPa in an Argon filled glove box. The pellet was sealed into an evacuated quartz tube, which was then slowly heated to 1448 K and kept at that temperature for 50 h.

Powder X-ray diffraction (XRD) was performed at room temperature using a D/Max-rA diffractometer with Cu-K<sub> $\alpha$ </sub> radiation and

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a graphite monochromator. Lattice parameters were refined by a least-squares fit using at least 30 XRD peaks. Quantum Design Physical Property Measurement System (PPMS-9) was used to perform the resistivity measurement. The dc magnetization measurement was performed in a Quantum Design Magnetic Property Measurement System (MPMS-5) under magnetic field H=10 Oe for the superconducting samples or 1000 Oe for measuring normal state susceptibility.

## 3. Results and discussion

The room-temperature XRD patterns of the representative CeFeAs<sub>1-x</sub>P<sub>x</sub>O<sub>0.95</sub>F<sub>0.05</sub> samples (x=0, 0.2 and 0.4) are shown in Fig. 1. For all the compounds, no obvious trace of impurity phases can be detected, and all the XRD peaks can be well indexed based on a tetragonal cell with the space group of P4/*nmm* (no. 129), indicating that all the samples are of high purity. Fig. 1(b) shows the variations of lattice constants *a* and *c* with P doping content *x*. Upon P doping, both *a* and *c* decrease monotonously. Further more, the lattice constants of the F and P co-doped systems are smaller than those of CeFeAs<sub>1-x</sub>P<sub>x</sub>O with identical *x*, suggesting the successful fluorine and phosphor doping. It can also be found from Fig. 1(b) that the *c*-axis shrinks more quickly than the *a*-axis does. This means that the chemical pressure could be anisotropic.

In Fig. 2, we present the temperature dependent resistivity of CeFeAs<sub>1-x</sub>P<sub>x</sub>O<sub>0.95</sub>F<sub>0.05</sub>. As is shown in Fig. 2(b), resistivity of CeFeAsO<sub>0.05</sub>F<sub>0.05</sub> decreases almost linearly as temperature decreases until an obvious upturn occurs below 100 K, which is reminiscent of the suppressed Fe<sup>2+</sup> AFM order and/or structure distortion. When temperature is further cooled down,  $\rho(T)$  shows a distinct decrease around 13.3 K and a sharp peak at 2.8 K. Intuitively the peak around 2.8 K is related to the Ce-4f AFM transition, similar to that of parent compound CeFeAsO [22]. This Ce-4f AFM order will be further confirmed by the temperature dependence of susceptibility whereafter (Fig. 3(b)). The measurement of magnetoresistance confirms that the drop around 13.3 K is due to SC transition (seeing Fig. 2(a)). The magnetic field broadens the SC transition region, and suppresses the SC transition temperature  $T_c^{onset}$  (defined as the temperature at which resistivity drops to 90% of the normal state) to a lower temperature. Upon 5% P doping, SC transition in resistivity becomes much more obvious, and  $T_c^{onset}$  increases to 17.4 K, but the resistance does



**Fig. 1.** Room-temperature XRD patterns of selected  $CeFeAs_{1-x}P_xO_{0.95}F_{0.05}$  (x=0, 0.2, and 0.4). Inset: Variations of lattice constants *a* (squares) and *c* (circles) with P doping content *x*. The solid symbols stand for data of  $CeFeAs_{1-x}P_xO_{0.95}F_{0.05}$ , while the open ones correspond to  $CeFeAs_{1-x}P_xO$ .



**Fig. 2.** Temperature dependent resistivity of CeFeAs<sub>1-x</sub>P<sub>x</sub>O<sub>0.95</sub>F<sub>0.05</sub>: (a) resistivity of CeFeAsO<sub>0.95</sub>F<sub>0.05</sub> under magnetic field  $\mu_0 H$  of 0, 0.1, 1, 3 and 5 T; (b)  $\rho$ -T curves of CeFeAs<sub>1-x</sub>P<sub>x</sub>O<sub>0.95</sub>F<sub>0.05</sub>; (c) the enlarged plot of  $\rho$ -T curves around the superconducting transition region.



**Fig. 3.** (a) Temperature dependence of magnetic susceptibility of CeFeAs<sub>1-x</sub>  $P_xO_{0.95}F_{0.05}$  (x=0, 0.05, 0.15, 0.3), measured under H=10 Oe, in ZFC (solid symbols) and FC (open symbols) protocols. Inset: enlarged plot of CeFeAsO<sub>0.95</sub> $F_{0.05}$  to show the AFM transitions of Ce<sup>3+</sup> ions and the kink induced by superconductivity. (b)  $\chi(T)$  and  $1/\chi(T)$  of CeFeAsO<sub>0.95</sub> $F_{0.05}$  measured under H= 1000 Oe, to show the Curie–Weiss behavior.

not drop to zero due to the reentrance caused by the Ce<sup>3+</sup> AFM order. As  $x \ge 0.1$ , zero resistance is finally observed, and  $T_c^{onset}$  reaches a maximum of 21.3 K at x=0.15.  $T_c^{onset}$  starts to decrease as x > 0.15.



**Fig. 4.** Phase diagram of CeFeAs<sub>1-x</sub> $P_xO_{0.95}F_{0.05}$  ( $0 \le x \le 0.4$ ).  $T_c^{onset}$  and  $T_c^{\chi}$  were obtained from the resistivity (onset point) and susceptibility (upturn point on  $d\chi/dT$ -T plot) measurements respectively, while  $T_N$  was determined by the peak position in the  $\chi$ -T curve. Lines are only guides to eyes.

The temperature dependence of dc magnetic susceptibility of  $CeFeAs_{1-x}P_xO_{0.95}F_{0.05}$  is shown in Fig. 3. For the compound CeFeAsO<sub>0.95</sub>F<sub>0.05</sub> without P doping, the Meissner effect is not obvious, and only a kink in susceptibility around 13 K can be found, confirming that it is on the boundary between AFM order of Fe ions and superconductor. Upon P doping, the diamagnetic screening effect becomes larger, and the volume fraction of magnetic shielding reaches to over 70% at the optimal P doping level x=0.15. To investigate the normal state properties of CeFeAs<sub>1-x</sub> $P_xO_{0.95}F_{0.05}$ , we performed the susceptibility measurement under H = 1000 Oe, and the result is presented in Fig. 3(b). The kink related to the SC transition observed under H = 10 Oe is now totally suppressed, and the  $\chi$ -*T* curve exhibits a good Curie–Weiss behavior above 150 K, with the fitted effective magnetic moment of  $2.48\mu_B$ , very close to the magnetic moment of free Ce<sup>3+</sup> ions  $(2.54\mu_B)$  calculated by the Hund's rule. As temperature is cooled down to 2.8 K, a peak related to the AFM order of Ce<sup>3+</sup> ions can be observed. We define the Ce-AFM transition temperature  $T_N$  as the peak position. It should be pointed out that in the whole P doping region ( $0 \le x \le 0.4$ ), the position of Ce<sup>3+</sup> AFM order does not change much on the  $\chi$ -T curve, i.e.,  $T_N$  remains nearly same with increasing P content x.

We summarize the phase diagram of SC and magnetism in CeFeAs<sub>1-x</sub>P<sub>x</sub>O<sub>0.95</sub>F<sub>0.05</sub> in Fig. 4. Chemical pressure introduced by P doping on the As site increases  $T_c^{onset}$  to a maximum of 21.3 K at x=0.15 and the  $T_c$ -x curve is also dome-like. In contrast to the variation of  $T_c$  with x,  $T_N$ , the AFM order temperature of Ce<sup>3+</sup> ions, only varies slightly with P doping content x. The chemical pressure enhancing SC could certainly be explained to be the consequence of the increase of the carrier concentration, however, there is still a problem: How does Kondo effect affect SC? Or in other words, why cannot this P doping chemical pressure induce SC in CeFeAs<sub>1-x</sub>P<sub>x</sub>O as other rare earth oxy-pnictides, but can enhance SC in CeFeAs<sub>1-x</sub>P<sub>x</sub>O<sub>0.05</sub>?

Since the valence of P is same as that of As, the partial substitution of As by P should not introduce any extra charge carriers to the system. Meanwhile, we note that the shrinkage of *a*-axis is only a fraction of that of the *c*-axis. Therefore we could draw such a conclusion that the change of the electronic state upon P doping is mainly ascribed to the shortening of the *c*-axis, or in other words, the pnictogen height, which is supported by the non-magnetic local density approximation (LDA) calculation [23,24]. On

one hand, in the CeFeAs<sub>1-x</sub> $P_x$ O system, we have demonstrated in our previous study that P doping weakens Fe<sup>2+</sup> AFM correlation, which will lead to the presence of  $x_{c_1}$  [20]; but on the other hand, inter-layer Kondo coupling (labeled by  $J_K$ ) and density of state at Fermi level (denoted by  $N(E_F)$ ) are simultaneously increased, which will consequently result in the sign-change of exchange interaction  $J_f = J_{RKKY} + J_f^0$ , where  $|J_{RKKY}| \sim |J_K N(E_F)|^2$  [25] and  $J_f^0 < 0$ , are the RKKY interaction and the exchange interaction in the absence of Kondo coupling, respectively, and is responsible to the evolution of AFM–FM of Ce-4*f* ground state at around  $x_{c_3}$ . SC was expected to be observed enclosing  $x_{c_1}$ , however since  $x_{c_3}$  is coincidently close to  $x_{c_1}$ , the strong Ce-4f spin fluctuation could make it difficult for conducting electrons to form Cooper pairs. In the case of the  $CeFeAs_{1-x}P_xO_{0.95}F_{0.05}$  system, however, according to the phase diagram figured by the study of neutron scattering [26], 5% F doping should suppress Fe<sup>2+</sup> AFM transition to about 50 K, thus intuitively,  $x_{c_1}$  would shift leftward to a much lower P doping level. It should be pointed out that the upturn on  $\rho(T)$  curve associated to the Fe<sup>2+</sup> AFM transition is hardly seen as x > 0.15, therefore it is mostly possible that the critical point  $x_{c_1}$  locates in the regime of x < 0.15. Furthermore, according to our results, the turning point  $x_{c_3}$  should persist to the regime with *x* larger than 0.4. This separation of the points  $x_{c_1}$  and  $x_{c_3}$  results in quenching of Fe<sup>2+</sup> AFM order at a region where Kondo effect is not prominent, and in this region enclosing  $x_{c_1}$ , SC should dominate. Therefore the effect of chemical pressure is to enhance SC; as P is further doped, Kondo effect is more and more evident, and thus SC is suppressed. The peculiar relation between SC and Kondo effect still needs to be clarified, and calls on a further investigation.

#### 4. Conclusion

In summary, we have investigated the effect of chemical pressure on CeFeAsO<sub>0.95</sub>F<sub>0.05</sub> by P doping on the As site. We found that the compound CeFeAsO<sub>0.95</sub>F<sub>0.05</sub> without P doping is on the boundary between AFM phase of Fe ions and superconductor, where the AFM order of Ce<sup>3+</sup> moment causes a reentrant behavior. In contrast to the previous reports on the effect of physical pressure on fluorine-doped system [11,13] where  $T_c$  is initially suppressed by pressure in the fluorine optimal-doped and over-doped regions,  $T_c$  of the CeFeAs<sub>1-x</sub>P<sub>x</sub>O<sub>0.95</sub>F<sub>0.05</sub> system initially increases with increasing chemical pressure, reaches a maximum of 21.3 K at x=0.15, and is finally suppressed to lower temperatures. Combined with previous reports, our studies suggest a competition between SC and Kondo effect, and highlight the importance of inter-layer Kondo physics in pnictides.

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