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To cite this article: Liling Sun et al 2010 EPL 91 57008

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Pressure-induced competition between superconductivity and Kondo effect in CeFeAsO_{1-x}F_x (x = 0.16 and 0.3)

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received 7 June 2010; accepted in final form 31 August 2010 published online 24 September 2010

PACS 74.70.-b – Superconducting materials other than cuprates PACS 62.50.-p – High-pressure effects in solids and liquids

Abstract – We studied high-pressure behavior of CeFeAsO_{1-x}F_x superconductors with x = 0.16and x = 0.3 by *in situ* measurements of electrical resistance, X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) with diamond anvil cell (DAC). A pressure-induced quantum phase transition from the superconducting state to the non-superconducting Kondo screened phase associated with a volume collapse was discovered in the layered CeFeAsO_{1-x}F_x compounds. The XAS data of Ce-L₃ in CeFeAsO_{0.7}F_{0.3} clearly show a spectral weight transfer from the main line to the satellite line after the transition, demonstrating that Ce's valence changes under high pressure. Comprehensive experimental results and analysis in this paper provide some insight into the connection among superconductivity, valence change and structural phase transition, which reveals a picture of pressure-induced competition between Kondo singlet and BCS singlet in the Ce-pnictide superconductors.

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Understanding the interplay between the RE 4felectrons (RE is a rare-earth element) and itinerant electrons in RE-containing superconductors is one of the important issues of current research in solid-state physics. Generally, physical pressure, chemical substitution or doping influence the interaction between the 4f-electrons and itinerant electrons. The transition from an itinerant to a localized state may lead to the formation of different competing phases. The system of $CeFeAsO_{1-x}F_x$ is one of the pnictide superconductors [1,2] which have a common layered crystal structure, belonging to the tetragonal P4/mmm space group at room temperature [2]. The itinerant electrons are confined to the FeAs structural units as conduction layers [3,4]. As to the parent compound CeFeAsO, it is not superconducting but shows an anomaly around 150K in resistivity and

magnetic susceptibility, respectively [2]. Recent studies [5,6] show that this anomaly is caused by the SDW instability. Superconductivity emerges after suppression of the SDW state by fluorine doping. It is surprisingly unusual that the superconducting transition temperature $(T_c = 41-46 \text{ K})$ of CeFeAsO_{1-x}F_x is much higher than that of conventional Ce-containing superconductors [7], which brings a great interest in understanding the physics in this new kind of superconductors.

Pressure can play an important role in the search for underlying physical mechanism of the competition among different quantum phases, because it can reduce the interatomic distance and thus change the state of electrons [8–11]. Recent X-ray absorption and photoemission spectroscopy studies on CeFeAsO_{1-x}F_x at ambient pressure show that Ce 4*f*-electrons are localized at ~ 1.7 eV below the Fermi level [12]. This result implies that pressure may induce many novel phenomena such as valence transition and Kondo effect in these compounds.

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Recently theoretical calculations on Ce-containing pnictide superconductors indicated that a competition between Kondo screening and superconductivity may take place when pressure is applied, which has been evidenced by an exponential increment of the Kondo temperature (T_K) , and pointed out that the rapid increase in T_K would destroy superconductivity due to the Kondo screening effect [13–16]. To date, for this prediction, there has not been an experimental observation of the actual pressure-induced full suppression of superconductivity in the Ce-containing pnictides. Here, we report an experimental finding of competition between superconductivity and Kondo effect in CeFeAsO $_{1-x}F_x$ through in situ measurements of high-pressure electrical resistance, X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). Our results indicate that the superconductivity of CeFeAsO_{1-x} F_x (x = 0.16 and 0.3) is suppressed at a pressure where an iso-structure phase transition occurs. By performing high-pressure XAS experiments, we found that Ce-L₃ absorption edge showed a clear satellite structure after the iso-structural phase transition. Comparing with the high-pressure data of cerium metal, we propose that the pressure-induced iso-structural phase transition in CeFeAsO_{1-x} F_x is of electronic origin. Namely it is driven by the Kondo screening effect between the 4f-electron of cerium and the conduction bands mainly from the 3d shell of iron.

The CeFeAsO_{1-x}F_x sample with x=0.16 was synthesized by the solid reaction method at ambient pressure [2]. To obtain more fluorine doping, the sample with x = 0.3 was synthesized under high pressure and high temperature [17]. The resulting samples were characterized by powder XRD with Cu $K\alpha$ radiation at room temperature. A nearly single phase with a common ZrCuSiAstype structure was achieved for both the samples. The lattice parameters for the x = 0.16 and x = 0.3 samples are a = 3.989 Å, c = 8.631 Å and a = 3.985 Å, c = 8.595 Å, respectively.

High pressures were generated using diamond anvils. The anvils with $300 \,\mu \text{m}$ flat were employed for all measurements in this study. In the resistance measurements, the standard four-probe technique was adopted, in which four $2\,\mu\mathrm{m}$ thick platinum leads are insulated from the preindented rhenium gasket by a thin layer of the mixture of cubic boron nitride and epoxy. The powder sample taken from a synthesized pellet was re-pressed into a flake and then the flake was loaded into a diamond anvil cell made of a Be-Cu alloy. The superconductivity transition of the sample at each loading point was measured using a closed-cycle refrigerator. High-pressure angle-dispersive XRD and high-pressure XAS experiments were carried out at room temperature at Beijing Synchrotron Radiation Facility and Shanghai Synchrotron Radiation Facility. In order to minimize X-ray absorption by the diamonds, partially perforated diamond anvils were used for XAS measurements in the transmission mode. The total thickness of the partially perforated anvils was reduced from



Fig. 1: (Colour on-line) (a) Electrical resistance as a function of temperature of the x = 0.3 sample. (b) Temperature dependence of dc magnetization of the x = 0.3 sample measured under 1 Oe after zero-field cooling and field cooling, respectively.

4.6 mm to 1 mm. The samples were loaded with the silicone fluid, because silicone fluid with initial viscosity of 1 cst can maintain the sample in a hydrostatic pressure environment up to 30 GPa [18]. Pressure was determined by ruby fluorescence [19].

We start from the electrical resistance and magnetization measurements for the samples investigated at ambient pressure. The temperature dependence of resistance and magnetization of the x = 0.3 sample is shown in fig. 1(a) and (b). It is seen that the sample has a bulk superconducting nature and its onset T_c is ~ 46 K. While the onset T_c of the x = 0.16 sample is ~ 41 K [2], indicating that more fluorine doping into the compound favors T_c enhancement.

In fig. 2(a) and (c), we present the temperature (T) dependence of the electrical resistance (R) of CeFeAsO_{1-x} F_x (x = 0.3 and 0.6) samples. It is found that the R-T curves of the both samples become broader and shift towards lower temperature with increasing pressure. Upon further uploading, the superconductivity is suppressed dramatically at 8.6 GPa for the x = 0.3sample and at 9.6 GPa for the x = 0.16 sample, and it disappears at 10 GPa and 12.8 GPa, respectively. When downloading from the highest pressure, we found that superconductivity can be recovered, as shown in fig. 2(b)and (d). We noted that the resistance of the samples studied did not display zero value under high pressure. To investigate the origin of the nonzero resistance of the compressed samples, the microstructure was imaged by using a scanning electron microscopy. Many micro-cracks were observed from the sample recovered from compression, as shown in the inset of fig. 2(b), suggesting that the nonzero resistance background at low temperature is likely caused by these micro-cracks.

To extract more information about the pressure effect on T_c , we plotted the onset T_c of the two samples vs.



Fig. 2: (Colour on-line) Temperature dependence of the normalized resistance $R/R_{80 \text{ K}}$ of CeFeAsO_{1-x}F_x samples at different pressures, showing data upon uploading (a), (c) and downloading (b), (d). A SEM image of the compressed sample with x = 0.3 is displayed in inset (b).

pressure in fig. 3. Here we define the onset T_c as the temperature where dR/dT rises rapidly. It is clearly seen that the T_c 's of the two samples decrease gradually when the pressure increases from ambient to $\sim 8 \,\mathrm{GPa}$, drop remarkably at 8.6 GPa (x = 0.3 sample) and 9.6 GPa (x =0.16 sample), and disappear at 10 GPa (x = 0.3 sample) and 12.8 GPa (x = 0.16 sample). For comparison, the results of the x = 0.12 sample measured by Zocco *et al.* [20] were plotted in fig. 3. The negative-pressure effect on T_c in the three samples is in good agreement below 8 GPa. The rate of decrease in T_c , however, varies for the sample with different fluorine doping level. It is likely that the T_c was suppressed more drastically in the sample with more fluorine doping. The negative effect of pressure on T_c in the CeFeAsO_{1-y} compound was also observed by Takeshita et al. [21], indicating that pressure has an equivalent effect on T_c for Ce-containing pnictides either with fluorine doping or oxygen vacancy. To get insight into the role of the Ce element in CeFeAsOF



Fig. 3: (Colour on-line) Pressure dependence of the T_c 's of CeFeAsO_{1-x}F_x (x = 0.16 and 0.3) samples. The data of the x = 0.12 sample is from ref. [20]. The inset shows $P(T_c)$ in SmFeAsO_{0.85}, LaFeAsO_{0.5}F_{0.5} and LaFeAsO_{0.89}F_{0.11}.

compounds, we compared the pressure dependence of T_c in SmFeAsO_{0.85}, LaFeAsO_{0.5}F_{0.5} and LaFeAsO_{0.89}F_{0.11} at the same pressure level [22–24]. T_c 's of (Sm, La)-containing superconductors decrease with pressure, as shown in inset of fig. 3, but are not suppressed to zero even at pressure up to 20 GPa, in sharp contrast to the high-pressure behavior of CeFeAsO_{1-x}F_x and CeFeAsO_{1-y} [21]. This suggests that cerium plays a special role for the T_c disappearance in CeFeAsO_{1-x}F_x.

We consider three possibilities which may tightly account for the observed phenomena. First, pressureinduced structural phase transition needs to be verified. Several investigations have been shown that the T_c can be suppressed when the crystal structure changes from one to the other [25,26]. Second, pressure-induced valence transition from Ce^{3+} to Ce^{4+} is an important factor because the transition may also suppress the T_c due to electron overdoping. Third, the Kondo effect caused by hybridization between the localized 4f-electrons and itinerant electrons in Ce-containing compounds is a possible issue to destroy superconductivity since high pressure can lead to a strong enhancement of the hybridization.

To investigate whether the disappearance of T_c in CeFeAsO_{1-x}F_x is related to a structural change, we performed *in situ* XRD measurements for the x = 0.16 and x = 0.3 samples in a diamond anvil cell at room temperature. No new feature was observed in the diffraction patterns under pressure up to 21 GPa for both samples, indicating that the crystal structure of the samples remains unchanged, in another word, still stays in a tetragonal form at pressure where the samples lost their superconductivity. The XRD results rule out the first possibility mentioned above. Then we estimated the pressure dependence of the volume change according to the lattice parameters, as shown in fig. 4. A clear discontinuity in the volume-pressure curves are found in the two



Fig. 4: (Colour on-line) Pressure dependence of the unit cell volume for the x = 0.16 and x = 0.3 samples.

samples, demonstrating that a first-order iso-structural phase transition occurred under high pressure. The volume collapses by 2.6(1)% at 8 GPa for the x = 0.16 sample and 2.1(1)% at 8.3 GPa for the x = 0.3 sample. The presence of the volume collapse at the pressure where the superconductivity is suppressed reflects a direct connection between them.

Further information was obtained by studying highpressure XAS at room temperature. We performed four separate XAS measurements on the $Ce-L_3$ absorption edge for the x = 0.3 sample. The pressure dependence of the Ce-L₃ edge of the sample is displayed in fig. 5(a). The position of the L₃-edge does not change with increasing pressure. However, the intensity of the main peak at 5.730 keV associated with the $4f^1$ configuration is suppressed when pressure is applied, while the intensity of a small satellite peak at 5.741 keV which has been attributed to the presence of the $4f^0$ configuration in the initial state appears increased at the same time. When the pressure is released from the maximum value to 4.5 GPa, the intensity of the main peak increases again whereas the intensity of the satellite decreases back to the lowpressure state, as seen in fig. 5(b), consistent with our resistance results in a similar pressure range where the superconductivity of the sample is recovered. Then we carefully investigated the pressure dependence of the mean valence (v) of Ce ions by using a widely used method, $v = 3 + I_{\text{satellite}} / (I_{\text{main}} + I_{\text{satellite}})$ [27,28], where I represents the amplitudes of the spectral peak, and found that v has a small change upon increasing pressure, varying from 3.0 at 1 GPa to 3.1 at 11.3 GPa.

Next, we compared our high-pressure XAS results with that of cerium metal. Figure 5(c) shows the L₃-XAS data of cerium metal together with its pressure dependence of the relative volume change [27,29]. Note that the highpressure behavior in CeFeAsO_{1-x}F_x resembles the γ - α phase transition under high pressure in cerium metal, in



Fig. 5: (Colour on-line) Ce-L₃ X-ray absorption spectrum of the x = 0.3 sample (a) upon uploading and (b) downloading, and (c) XAS data of the γ and α phases in cerium metal together with the pressure dependence of atomic volume change.

the latter case a similar satellite peak at the same relative position to the main peak emerges only in the α -phase, revealing that the spectra weight transfer is tightly associated with the γ - α phase transition. XRD measurements on cerium metal showed that the volume collapses about 15% after iso-structural γ - α phase transition [29]. The mechanism of the γ -to- α transition in cerium metal has been debated in the literature for a long time. Several scenarios have been proposed to explain the electronic origin of this transition, including valence change, Mott transition, and Kondo effect etc. Among them, the Kondo Volume Collapse (KVC) scenario received more attention, and there are more and more evidences that support KVC from both numerical simulations and experiments [27,30-32]. The similarity of the iso-structural transition and spectra weight transfer of cerium ions in $CeFeAsO_{1-x}F_x$ to cerium metal implies that the KVC scenario may be applied to $CeFeAsO_{1-x}F_x$ system. We thus propose that the full suppression of superconductivity under high pressure in $CeFeAsO_{1-x}F_x$ is possibly caused by Kondo effect.

In KVC, the important difference between the α -phase and the γ -phase in cerium metal is their Kondo temperatures. Numerical simulation and experiments [27,30–32] indicated that the Kondo temperature of cerium metal is above 1000 K in the α -phase and negligible in the γ -phase. Though our high-pressure XRD and XAS measurements were carried out at room temperature, we still can observe a similar behavior in CeFeAsO_{1-x}F_x to cerium metal, we thus anticipate that the Kondo temperature of the CeFeAsO_{1-x}F_x should be higher than room temperature.

In summary, pressure-induced full suppression of superconductivity in CeFeAsO_{1-x}F (x = 0.16 and 0.3) is found by *in situ* resistance measurements with a diamond anvil cell. Based on the analysis of high-pressure XRD and XAS experimental results, we propose that the disappearance of T_c in CeFeAsO_{1-x}F is due to a competition between superconducting phase and Kondo screened phase under high pressure. A clearer physical picture can be described as follows: the formation of the Kondo singlet between Ce local moments and Fe 3*d*-electrons would break Cooper pairs in the FeAs layers, and then kill the superconductivity. Furthermore, our study reveals that doping concentration of fluorine in CeFeAsO_{1-x}F influences the critical pressure of T_c disappearance, *i.e.* more fluorine doping shifts the critical pressure to a lower side.

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We sincerely thank J. Y. MA and S. Q. GU of SSRF for help with the XAS experiment. The authors wish to thank the National Science Foundation of China for its support of this research through Grant Nos. 10874230, 10874211, 10804127 and 11074294. This work was also supported by the 973 project (2010CB923000) and the Chinese Academy of Sciences.

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