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Superconductivity at 41 K and Its Competition with Spin-Density-Wave Instability in Layered $CeO_{1-x}F_xFeAs$

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A series of layered $CeO_{1-x}F_xFeAs$ compounds with $x = 0$ to 0.20 are synthesized by the solid state reaction method. Similar to the LaOFeAs, the pure CeOFeAs shows a strong resistivity anomaly near 145 K, which was ascribed to the spin-density-wave instability. F doping suppresses this instability and leads to the superconducting ground state. Most surprisingly, the superconducting transition temperature could reach as high as 41 K. Such a high T_c strongly challenges the classic BCS theory based on the electron-phonon interaction. The closeness of the superconducting phase to the spin-density-wave instability suggests that the magnetic fluctuation plays a key role in the superconducting pairing mechanism. The study also reveals that the Ce $4f$ electrons form local moments and are ordered antiferromagnetically below 4 K, which could coexist with superconductivity.

The recent discovery of superconductivity with a transition temperature of 26 K in $LaO_{1-x}F_xFeAs$ system [1] has generated tremendous interest in the scientific community. Besides a relatively high transition temperature, the system displays many interesting properties. Among others, the presence of competing ordered ground states is one of the most interesting phenomena [2]. The pure LaOFeAs itself is not superconducting but shows an anomaly near 150 K in both resistivity and dc magnetic susceptibility [1]. This anomaly was shown to be caused by the spin-density-wave (SDW) instability [2–4]. Electron doping by F suppresses the SDW instability and yields the superconductivity. Here we show that similar competing orders exist in another rare-earth transition metal oxypnictide $Ce(O_{1-x}F_x)FeAs$. Most surprisingly, the superconducting transition temperature in this system could reach as high as 41 K. Except for cuprate superconductors, T_c in such iron-based compounds has already become the highest.

The rather high superconducting transition temperature has several important implications. First, the electron-phonon interaction needs to be carefully examined. There have been several first-principle calculations indicating that the electron-phonon coupling is not strong enough to explain the superconductivity in $LaO_{1-x}F_xFeAs$ [5–7]. However, an opposite opinion also exists [8]. The substantially higher T_c here poses a more serious challenge to the classic phonon-mediated pairing mechanism. Second, the rare-earth Ce-based compounds usually show hybridization between the localized f electrons and itinerant electrons. This often leads to a strong enhancement of carrier effective mass at low temperature. Even for $4d$ transition metal oxypnictide with the same type of structure as CeOFeAs, a recent report indicates that the electronic specific heat coefficient of Ce-based CeORuP ($\gamma = 77$ mJ/mol K²) is 20 times higher than the value of La-

based LaORuP ($\gamma = 3.9$ mJ/mol K²) [9]. The hybridization tends to cause various ordered states at low temperature, like ferromagnetic (FM) or antiferromagnetic (AFM) ordering. Although the superconducting state could occur in Ce-based materials, the superconducting transition temperature is usually very low. The highest superconducting transition temperature is only 6.1 K achieved in $CeRu_2$ [10]. The very high superconducting transition temperature obtained here on $Ce(O_{1-x}F_x)FeAs$ offers an opportunity to examine the role played by Ce $4f$ electrons. Third, the superconducting phase is very close to the spin-density-wave instability. This indicates that the magnetic fluctuation plays a key role in the superconducting pairing mechanism.

A series of layered $CeO_{1-x}F_xFeAs$ compounds with $x = 0$, 0.04, 0.08, 0.12, 0.16, and 0.20 are synthesized by the solid state reaction method using CeAs, Fe, CeO_2, CeF_3, Fe_2As as starting materials. CeAs was obtained by reacting Ce chips and As pieces at 500 °C for 15 h and then 850 °C for 5 h. The raw materials were thoroughly mixed and pressed into pellets. The pellets were wrapped with Ta foil and sealed in an evacuate quartz tube. They were then annealed at 1150 °C for 50 h. The resulting samples were characterized by a powder x-ray diffraction (XRD) method with Cu $K\alpha$ radiation at room temperature. The XRD patterns for the parent ($x = 0$) and $x = 0.16$ compounds are shown in Fig. 1, which could be well indexed on the basis of tetragonal ZrCuSiAs-type structure with the space group $P4/nmm$. A tiny extra (impurity) peak at $2\theta \approx 27°$ is observed only in F-doped sample. The lattice parameters for the parent and $x = 0.16$ compounds obtained by a least-square fit to the experimental data are $a = 3.996$ Å, $c = 8.648$ Å, and $a = 3.989$ Å, $c = 8.631$ Å, respectively. Compared to the undoped phase CeOFeAs, the apparent reduction of the lattice volume upon F doping indicates a successful chemical substitution. A careful
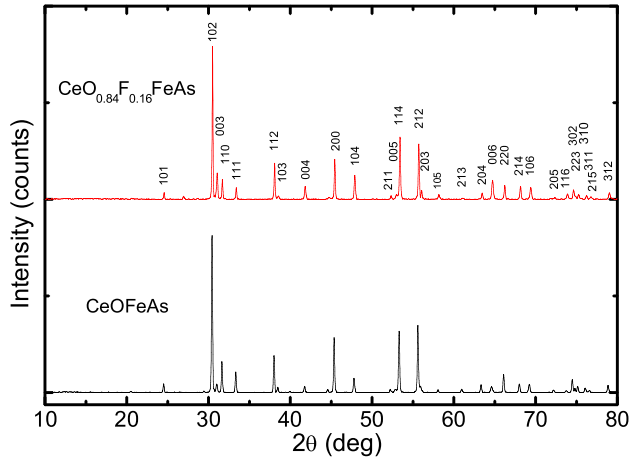
FIG. 1 (color online).   X-ray powder diffraction patterns of the pure CeOFeAs and $CeO_{0.84}F_{0.16}FeAs$ compounds.

inspection of the two XRD patterns in Fig. 1 also reveals some differences in the peak intensities for the two samples. As we found that fluorine doping reduces the reaction temperature, the grain sizes are expected to be larger in the F-doped samples. This may explain the enhanced intensities of refractions from certain crystalline planes.

Standard 4-probe dc resistivity and ac susceptibility measurements were preformed down to 1.8 K in a Physical Property Measurement System (PPMS) of Quantum Design company. Figure 2(a) shows the temperature dependence of the resistivity. The pure CeOFeAs sample has rather high dc resistivity value. The resistivity increases slightly with decreasing temperature, but below roughly 145 K, the resistivity drops steeply. After F doping, the overall resistivity decreases and the 145 K anomaly shifts to lower temperature and becomes less pronounced. At higher F doping, the anomaly disappears and a superconducting transition occurs. The highest T_c (41 K) is obtained at $x = 0.16$, which can be seen clearly from an expanded plot of the temperature-dependent resistivity curve [Fig. 2(b)]. T_c drops slightly with further F doping. The bulk superconductivity in F-doped CeOFeAs is confirmed by dc magnetic susceptibility measurements. Figure 2(c) shows the real part χ' of ac susceptibility in a temperature range near T_c for the $x = 0.16$ sample. The superconducting volume fraction is estimated to be about 60%. Figure 3(a) is the phase diagram showing the resistivity anomaly, i.e., SDW transition (circle) and superconducting transition (square) temperatures as a function of F content.

An important parameter to characterize superconductivity is the upper critical field $H_{c2}(0)$. In our earlier study on $LaO_{0.9}F_{0.1-\delta}FeAs$ superconductor with an onset $T_c = 26$ K, we already found a rather high upper critical field $H_{c2}(0)$ over 50 T [11]. Here we would expect much higher $H_{c2}(0)$ in Ce-based compounds owing to their substantially higher T_c. We measured the temperature-dependent resis-
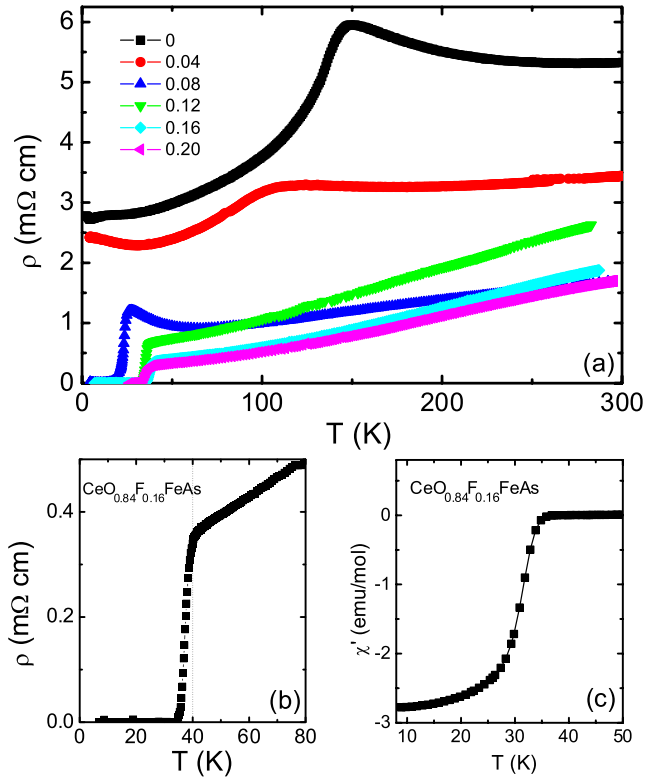

FIG. 2 (color online).   (a) The electrical resistivity vs temperature for a series of $CeO_{1-x}F_xFeAs$. (b) T-dependent resistivity in an expanded region for $x = 0.16$ sample. The superconducting transition with sharp onset temperature at 41 K is seen. (c) Real part of T-dependent ac magnetic susceptibility.

tivity of a $x = 0.12$ sample with T_c onset close to 40 K under different magnetic fields. As shown in Fig. 3(b), T_c was suppressed only by several Kelvins at 14 T (which is the highest magnetic field available in our PPMS system). A precise determination of $H_{c2}(0)$ apparently requires measurement under much higher field [11].

The resistivity behavior of the pure CeOFeAs is very similar to that of LaOFeAs, except that a resistivity upturn was observed in the later compound at low temperature. As we demonstrated earlier, the anomaly at 150 K is caused by spin-density-wave instability, and a gap opens below the transition temperature due to the Fermi surface nesting [2]. To confirm the same origin for the anomaly, we performed infrared measurement on Bruker 66 v/s spectrometer in the frequency range from 40 cm^{-1} to 15 000 cm^{-1} at different temperatures, and derived the conductivity from Kramers-Kronig transformations. Figure 4 shows the reflectance and conductivity spectra in a far-infrared region. As expected, CeOFeAs shares very similar optical response behavior as LaOFeAs. Most notably, the reflectance below 400 cm^{-1} is strongly suppressed at low frequency below the phase transition temperature, which is a strong indication for the formation of an energy gap. However, the low-frequency reflectance still increases fast towards unity
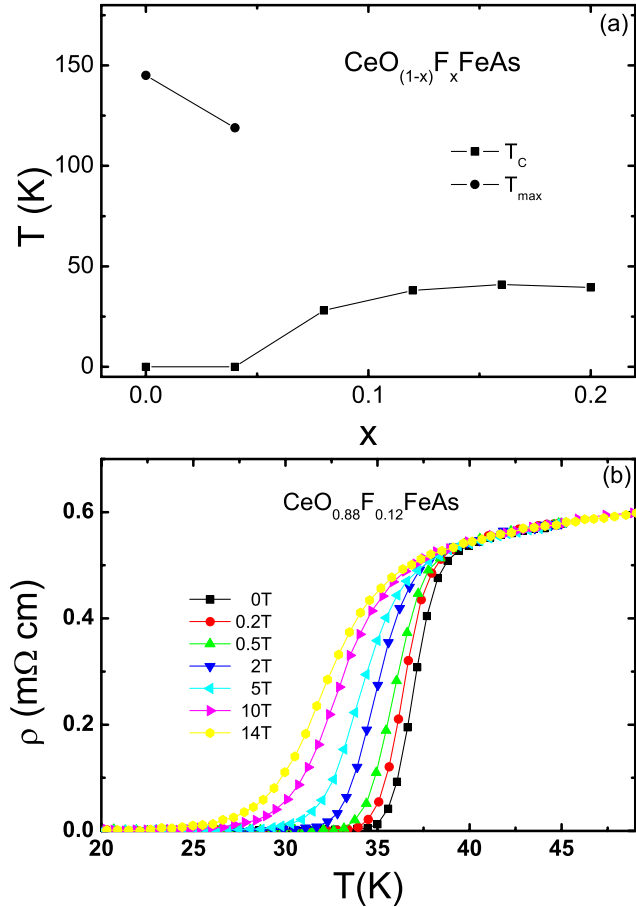
FIG. 3 (color online). (a) The phase diagram showing the anomaly (circle) and superconducting transition (square) temperatures as a function of F content. (b) The resistivity vs temperature curves under selected magnetic fields.
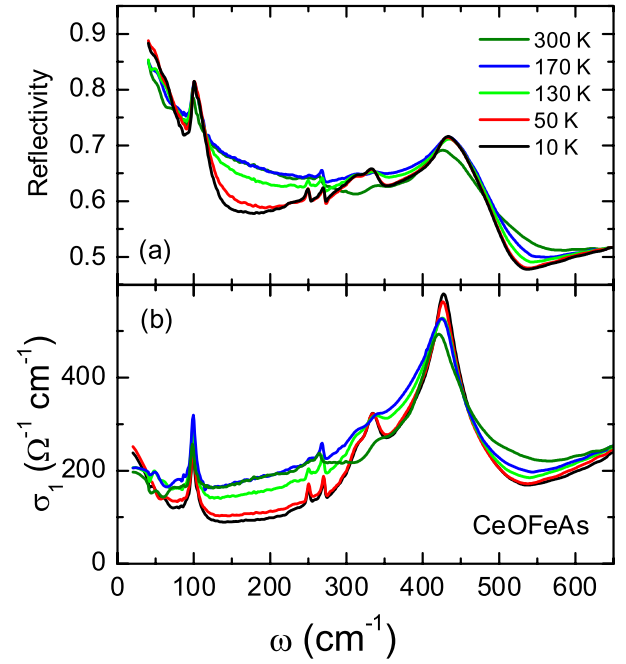

FIG. 4 (color online). The reflectance (a) and conductivity (b) spectra in the far-infrared region at different temperatures for the pure CeOFeAs sample.

at zero frequency, indicating a metallic behavior even below the phase transition, being consistent with the dc resistivity measurement which reveals an enhanced conductivity. The data indicate clearly that the Fermi surfaces are only partially gapped.

We notice that, among different reported superconducting systems in such layered transition metal oxypnictides, the $LaO_{1-x}F_xFeAs$ and $CeO_{1-x}F_xFeAs$ systems share remarkably similar character: the presence of competing ground states. When the SDW order is destroyed by electron doping, superconductivity could occur at a much higher temperature. This gives a hint on how to search for materials with potentially higher T_c. The interplay between superconductivity and spin-density-wave instability is thus of central interest in those systems.

To get insight into whether the rare-earth element Ce $4f$ electrons hybridize with the itinerant Fe $3d$ electrons at low temperature, we measured the low-T specific heat. To our surprise, another magnetic ordering was revealed in those Ce-based samples. Figure 5(a) shows the plot of C/T as a function of temperature for pure CeOFeAs at $H = 0$ and

5 T, and 16% F-doped sample ($CeO_{0.84}F_{0.16}FeAs$) at $H = 0$, respectively. For nonsuperconducting CeOFeAs, a sharp λ-shape peak at 3.7 K is observed under zero magnetic field. The peak shifts to 2.8 K under a magnetic field of 5 T. This clearly indicates that a long-range antiferromagnetic ordering occurs at low temperature. There is a very weak effect in dc resistivity at the AFM transition temperature. For LaOFeAs without the rare-earth $4f$ electrons, there is no such specific heat anomaly at low temperature [2], indicating unambiguously that the AFM transition for CeOFeAs is originated from the ordering of Ce $4f$ moments. No significant enhancement of electronic specific coefficient is observed from the high T specific heat. We also measured the dc magnetic susceptibility of the parent CeOFeAs sample in the PPMS system; the data are shown in Fig. 5(b). By fitting the data with the Curie-Weiss law, $\chi(T) = \chi_0 + C/(T + \theta)$, where χ_0 is a temperature independent susceptibility, C the Curie constant, and θ the Curie-Weiss temperature. The obtained effective magnetic moments per formula unit is 2.43 μ_B, which is close to the magnetic moment of free Ce3+ ion. The sharp drop below 4 K here is also due to the AFM ordering (Néel temperature) of Ce $4f$ electrons, consistent with specific heat data.

For the 16% F doped superconducting sample, we also observe the onset signature of the AFM ordering down to 1.8 K, the lowest measured temperature. Then, the AFM transition must occur below this temperature. The data strongly suggest that the high-temperature superconductivity coexists with the AFM ordering of Ce $4f$ local mo-
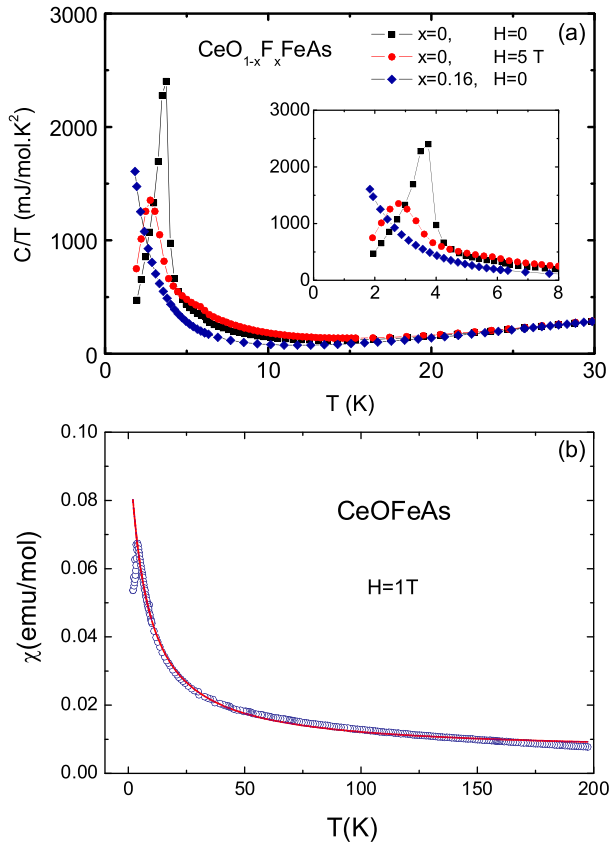
FIG. 5 (color online). (a) The plot of C/T vs T for the pure CeOFeAs sample at $H = 0$ and 5 T, and the $CeO_{0.84}F_{0.16}FeAs$ sample at $H = 0$, respectively. The inset shows the plot in an expanded low temperature range. (b) The T-dependent magnetic susceptibility of pure CeOFeAs sample. The red (or gray) curve is a fit to the Curie-Weiss law. The sharp drop below 4 K is due to AFM ordering.

ments. This coexistence implies that the exchange interaction between the Ce $4f$ moments and the itinerant Fe $3d$ electrons is very weak. So, there is no appreciable mixing or hybridization between them in the present systems.

To summarize, we have synthesized a series of rare-earth based transition metal oxypnictide $CeO_{1-x}F_xFeAs$ compounds. The superconducting transition temperature could be as high as 41 K. This very high superconducting transition temperature strongly challenges the pairing mechanism based on the electron-phonon interaction. Similar to the LaOFeAs, the pure CeOFeAs shows a strong resistivity anomaly near 145 K, which was ascribed to the spin-

density-wave instability. *F* doping suppresses this instability and leads to the superconducting ground state with rather high T_c. The very interesting interplay between the superconducting phase and the spin-density-wave instability strongly suggests that the magnetic fluctuation plays a key role in the superconducting pairing mechanism. Furthermore, the study reveals that the Ce $4f$ electrons form local moments and ordered antiferromagnetically below 4 K which could coexist with superconductivity.

Note added.—After we completed this work, we learned of an independent work on another rare-earth Sm-based superconductor $SmFeAsO_{1-x}F_x$ ($x = 0.1$) by Chen *et al.* [12].

[1] Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. **130**, 3296 (2008).
[2] J. Dong, H. J. Zhang, G. Xu, Z. Li, G. Li, W. Z. Hu, D. Wu, G. F. Chen, X. Dai, J. L. Luo, Z. Fang, and N. L. Wang, arXiv:0803.3426 (unpublished).
[3] C. de la Cruz, Q. Huang, J. W. Lynn, J. Li, W. Ratcliff, II, J. L. Zarestky, H. A. Mook, G. F. Chen, J. L. Luo, N. L. Wang, and P. Dai, arXiv:0804.0795 (unpublished).
[4] M. A. McGuire, A. D. Christianson, A. S. Sefat, R. Jin, E. A. Payzant, B. C. Sales, M. D. Lumsden, and D. Mandrus, arXiv:0804.0796 (unpublished).
[5] K. Haule, J. H. Shim, and G. Kotliar, arXiv: 0803.1279 [Phys. Rev. Lett. (unpublished)].
[6] L. Boeri, O. V. Dolgov, and A. A. Golubov, arXiv: 0803.2703 (unpublished).
[7] I. I. Mazin, D. J. Singh, M. D. Johannes, and M. H. Du, arXiv: 0803.2740 (unpublished).
[8] H. Eschrig, arXiv: 0804.0186 (unpublished).
[9] C. Krellner, N. S. Kini, E. M. Brüning, K. Koch, H. Rosner, M. Nicklas, M. Baenitz, and C. Geibel, Phys. Rev. B **76**, 104418 (2007).
[10] T. Matthias, H. Suhl, and E. Corenzwit, Phys. Rev. Lett. **1**, 449 (1958).
[11] G. F. Chen, Z. Li, G. Li, J. Zhou, D. Wu, J. Dong, W. Z. Hu, P. Zheng, Z. J. Chen, J. L. Luo, and N. L. Wang, arXiv:0803.0128 (unpublished).
[12] X. H. Chen *et al.*, arXiv:0803.3603v1.