

Iron-Based Layered Superconductor La[O_{1-x}F_x]FeAs ($x = 0.05-0.12$) with $T_c = 26$ K

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Discovery of the copper-based superconductor La_{2-x}Ba_xCuO₄¹ with a high transition temperature (T_c) triggered extensive research with the intention of developing new transition-metal-based superconductors.^{2,3} Currently, high T_c superconductors are limited to layered perovskites that contain CuO₂ structural units as the conduction layers. However, the T_c of the non-Cu-based superconductors in this category has remained low, although spin triplet superconductivity has been found in UPt₃ ($T_c \sim 0.54$ K)⁴ and Sr₂RuO₄ ($T_c \sim 1.4$ K).^{5,6} Here, we report a layered iron-based compound, LaOFeAs, which undergoes superconducting transition under doping with F⁻ ions at the O²⁻ site. Its T_c exhibits a trapezoidal shape dependence on F⁻ content, with the highest T_c of ~ 26 K at 5–11 atom %. Further, its magnetic susceptibility indicates that F-doped LaOFeAs exhibits Curie–Weiss-like behavior in the normal conducting state.

We have been studying several quaternary oxypnictides, LaOMP_n (M = Mn, Fe, Co, and Ni; P_n = P and As),^{7–10} leading to the discovery of the Fe and Ni based superconductors, LaOFeP ($T_c \sim 5$ K)⁸ and LaONiP ($T_c \sim 3$ K).⁹ LaOFeAs, a member of LaOMP_n, has a layered crystal structure belonging to the tetragonal *P4/nmm* space group. As shown in Figure 1a, the unit cell contains two molecules, and the chemical formula is represented by (La₂O₂)(Fe₂As₂). The Fe₂As₂ layer, which is sandwiched between the La₂O₂ layers, serves as a carrier conduction path.^{8–11} Thus, conduction carriers are two-dimensionally confined in the Fe₂As₂ layer, causing strong interactions among the electrons. Further, aliovalent ion doping in the insulating La₂O₂ layer, for instance, the replacement of O²⁻ with F⁻, may provide an extra positive charge in the insulating layer and a negative charge in the conduction layer. This would lead to the modulation of the interactions through the change in carrier density, without seriously exerting crystallographic defects in the conduction layer.

Polycrystalline LaOFeAs was synthesized by heating a mixture of lanthanum arsenide, iron arsenide, and dehydrated La₂O₃ powders in a silica tube filled with Ar gas at 1250 °C for 40 h, a procedure similar to that employed for LaOFeP.⁸ Ca²⁺ and F⁻ ion doping was performed by adding CaO and a 1:1 mixture of LaF₃ and La, respectively, to the starting material. The crystal structure, phase purity, and lattice constants of the resulting powders were examined by powder X-ray diffraction (XRD; Bruker D8 Advance TXS) using Cu K α radiation from a rotating anode with the aid of Rietveld refinement using Code TOPAS3.¹² DC electrical resistivity was measured by a four-probe technique using silver paste electrodes at temperatures of 1.8 to 300 K. Magnetization measurements were performed with a vibrating sample magnetometer (VSM; Quantum

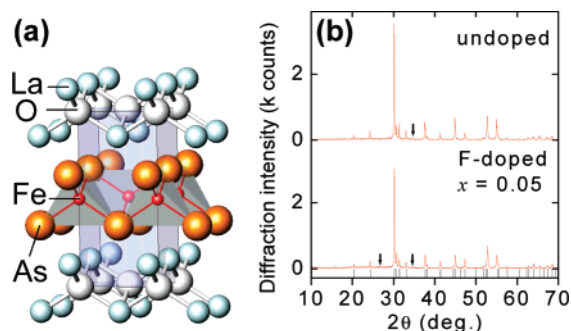


Figure 1. (a) Crystal structure of LaOFeAs. (b) Powder XRD patterns of undoped LaOFeAs and La[O_{1-x}F_x]FeAs: $x = 0.05$. Black bars at bottom show calculated Bragg diffraction positions of LaOFeAs. Arrows denote peaks due to impurity phases, FeAs (helimagnetic),¹³ and LaOF.

Design) in the same temperature range. Figure 1b shows typical powder XRD patterns of undoped and 5 atom % F-doped LaOFeAs.

All the peaks are assigned the same as those for the LaOFeAs phase, except some weak peaks that were assigned to impurity phases,¹³ indicating that the samples are mostly composed of a single phase. The LaOFeAs phase is tetragonal with room-temperature lattice constants of $a = 0.403552(8)$ nm and $c = 0.87393(2)$ nm for the undoped samples and $a = 0.40320(1)$ nm and $c = 0.87263(3)$ nm for the 5 atom % F-doped samples. The lattice constants decrease systematically with nominal dopant concentration by F⁻ substitution to the site of O²⁻ ions. The contents of the dopant (x) were determined by the lattice constants using Vegard's volume rule.¹⁴ Figure 2a shows the temperature (T) dependences of electrical resistivity (ρ) and magnetic molar susceptibility (χ_{mol}) for undoped and F-doped LaOFeAs samples. The ρ - T curve for the undoped LaOFeAs sample exhibits a sudden decrease at ~ 150 K (T_{anom}). With a further decrease in temperature below T_{anom} , ρ continues to decrease and then increases, showing a minimum at ~ 100 K (T_{min}). F-doped samples (3, 4, and 5 atom %) also show T_{min} , whose values were lowered with the F⁻ content. However, the minimum disappears in 11 and 12 atom % F-doped samples. It is noteworthy that, with a further decrease in T , the ρ - T curves in the samples with F⁻ content more than 4 atom % show abrupt drops to zero at 5–22 K depending on the F⁻ content, while the undoped and 3 atom % F-doped samples never exhibit zero resistivity.

As shown in Figure 2b, χ_{mol} for the 5 atom % F-doped sample starts to decrease at ~ 25 K and shows large negative values with the lowering of T . On the other hand, χ_{mol} for the undoped sample shows positive values in the entire temperature range examined. The zero resistivity and the large diamagnetic susceptibility indicate that LaOFeAs becomes a superconductor by F-doping.

The volume fraction of the superconducting (SC) phase estimated from the observed diamagnetic susceptibility is $\sim 50\%$, confirming

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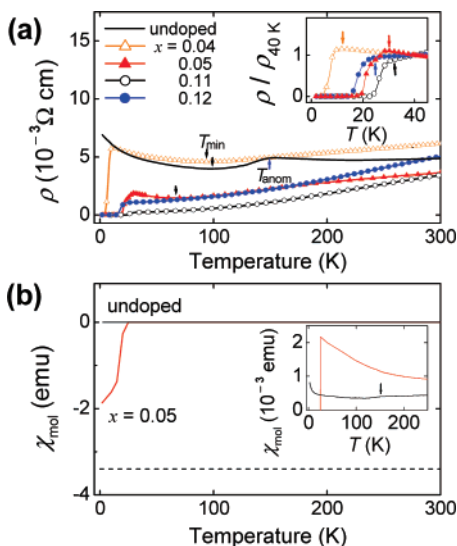


Figure 2. (a) Electrical resistivity (ρ) versus temperature (T) for undoped and $\text{La}[\text{O}_{1-x}\text{F}_x]\text{FeAs}$: $x = 0.04, 0.05, 0.11,$ and 0.12 . Inset shows expanded ρ - T curves for $x = 0.04, 0.05, 0.11,$ and 0.12 . Arrows show onset transition temperatures. (b) Molar susceptibility (χ_{mol}) versus T for undoped and $\text{La}[\text{O}_{1-x}\text{F}_x]\text{FeAs}$: $x = 0.05$. The dotted line denotes perfect diamagnetism for the sample. Inset shows expanded χ_{mol} - T curves at 10^3 times magnification of the vertical axis. An arrow shows T_{anom} in part a.

that the superconductivity is due to the F-doped LaOFeAs phase. Further, T_c was not observed for Ca^{2+} -doped samples, suggesting that a critical factor for induction of superconductivity is electron doping, and not hole doping. The inset in Figure 2b shows an expanded graph of χ_{mol} - T , in which the vertical axis is magnified 10^3 times compared to that of Figure 2b. The χ_{mol} values of both samples were $\sim 10^{-3}$ at room temperature, which are much larger than those of the 3d electron based superconductors, e.g., $\sim 10^{-4}$ for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.¹⁵ The χ_{mol} value in the normal conducting (NC) state that was enhanced by the F^- ions, increased with lowering T , exhibiting Curie–Weiss-like behavior.

Figure 3 summarizes T_{anom} , T_{min} , and T_c as a function of F^- content, with the onset transition temperature (T_{onset}) in each sample also shown. It is evident that F-doping induces the superconducting phase in LaOFeAs and the highest T_c of ~ 26 K ($T_{\text{onset}} > 30$ K) is attained at the F^- content of ~ 11 atom %. On the other hand, T_{min} , which was significantly sensitive to sample preparation for the undoped composition, tends to monotonically decrease with increasing F^- content up to ~ 11 atom %, and it seems to merge with T_c with further F-doping. Such variation appears to be analogous to that of the spin gap in underdoped Cu based superconductors.¹⁶ Further, T_{anom} observed in undoped LaOFeAs and 3 atom % F-doped samples disappeared in the superconducting samples, implying a relation with the occurrence of superconductivity, although its origin remains unclear at present. F-doping makes the number (6) of Fe 3d electrons closer to that (7) of Co 3d electrons in metallic LaOCOPn , which becomes ferromagnetic below ~ 65 K,¹⁰ suggesting that the superconducting phase is located close to the ferromagnetic phase. In summary, the electrical

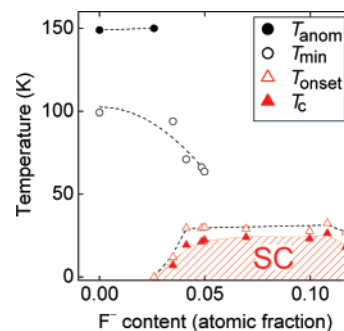


Figure 3. T_c , T_{onset} , and T_{min} in the ρ - T curves as a function of F^- content (x) for $\text{La}[\text{O}_{1-x}\text{F}_x]\text{FeAs}$. T_c is defined as the temperature where the ρ value becomes half of that at T_{onset} . T_{anom} values for the undoped and $\text{LaO}_{0.97}\text{F}_{0.03}\text{FeAs}$ are also shown. Dotted curves are guides for eyes.

conductivity and magnetization measurements demonstrate that the F^- ion-doped layered LaOFeAs is a bulk superconductor. T_c changes with F^- content, exhibiting a maximum T_c of ~ 26 K at a F^- content of ~ 11 atom %. Further, the ρ - T curve in the normal conducting state shows a minimum in the underdoped region. Although further research is needed to examine origins of the T_{anom} , T_{min} , and the high T_c , the present results demonstrate that the layered oxypnictide, LnOMPn is a promising new platform to realize high T_c superconductors.

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Supporting Information Available: Crystal structure data of LaOFeAs at room temperature. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Bednorz, J. G.; Müller, K. A. *Z. Phys.* **1986**, *B64*, 189.
- (2) Takada, K.; Sakurai, H.; Takayama-Muromachi, E.; Izumi, F.; Dilanian, R. A.; Sasaki, T. *Nature* **2003**, *422*, 53.
- (3) Meisner, G. P. *Phys. B and C* **1981**, *108*, 763.
- (4) Stewart, G. R.; Fisk, Z.; Willis, J. O.; Smith, J. L. *Phys. Rev. Lett.* **1984**, *52*, 679.
- (5) Maeno, Y.; Hashimoto, H.; Yoshida, K.; Nishizaki, S.; Fujita, T.; Bednorz, J. G.; Lichtenberg, F. *Nature* **1994**, *372*, 532.
- (6) Ishida, K.; Mukuda, H.; Kitaoka, Y.; Asayama, K.; Mao, Z. Q.; Mori, Y.; Maeno, Y. *Nature* **1998**, *396*, 658.
- (7) Quebe, P.; Terbuchte, L. J.; Jeitschko, W. *J. Alloys Compd.* **2000**, *302*, 72.
- (8) Kamihara, Y.; Hiramatsu, H.; Hirano, M.; Kawamura, R.; Yanagi, H.; Kamiya, T.; Hosono, H. *J. Am. Chem. Soc.* **2006**, *128*, 10012.
- (9) Watanabe, T.; Yanagi, H.; Kamiya, T.; Kamihara, Y.; Hiramatsu, H.; Hirano, M.; Hosono, H. *Inorg. Chem.* **2007**, *46*, 7719.
- (10) Yanagi, H.; Kawamura, R.; Kamiya, T.; Kamihara, Y.; Nakamura, T.; Osawa, H.; Hosono, H. Submitted for publication.
- (11) Lebegue, S. *Phys. Rev. B* **2007**, *75*, 035110.
- (12) *TOPAS, version 3*; Bruker AXS: Karlsruhe Germany, 2005.
- (13) Selte, K.; Kjekshus, A.; Andresen, A. F. *Acta Chem. Scand.* **1972**, *26*, 3101.
- (14) Cox, A.; Sangster, M. J. L. *J. Phys. C: Solid State Phys.* **1985**, *18*, L1123.
- (15) Takagi, H.; Ido, T.; Ishibashi, S.; Uota, M.; Uchida, S.; Tokura, Y. *Phys. Rev. B* **1989**, *40*, 2254.
- (16) Takenaka, K.; Mizuhashi, K.; Takagi, H.; Uchida, S. *Phys. Rev. B* **1994**, *50*, 6534.

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